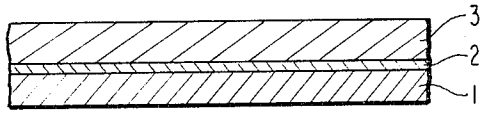
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PROCESS FOR THE MANUFACTURE OF AN ELECTROPHOTOGRAPHIC SENSITIVE MATERIAL

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PROCESS FOR THE MANUFACTURE OF AN ELECTROPHOTOGRAPHIC SENSITIVE MATERIAL

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ABSTRACT OF THE DISCLOSURE

An electrophotographic sensitive material wherein a reaction product of synthetic resin having OH-groups and a chromium compound is interposed as an intermediate layer between a photoconductive image-forming layer and a support, such as paper, plastic sheet, thin metallic film and the like and a process for the manufacture thereof.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to an electrophotographic sensitive material, more especially an electrophotographic copying paper and offset master blank and a process for the manufacture thereof.

(2) Description of the prior art

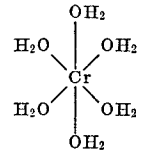
An electrophotographic sensitive material has been previously manufactured by directly coating the surface of a support, such as paper, plastic sheet, thin metallic film and the like, which has been subjected to a resistance lowering treatment with quaternary ammonium salts and the like, with a paint in which a fine photoconductive powder, a sensitizer and the like are dispersed in a film-forming and electrically insulating resin, to form a photoconductive image-forming light, developed and fixed to form an image. In an attempt to strengthen the adhesion between the support and the image-forming layer and to improve the printing durability thereof, epoxy resin has been interposed as an intermediate layer between the support and the image-forming layer. However, the results of this approach have not been completely satisfactory.

This invention relates to the further improvement of such a material by interposing the reaction product of a resin containing OH-groups and a chromium compound between the support and the photoconductive image-forming layer.

That is to say, the object of this invention is to produce an electrophotographic sensitive material, more particularly, an electrophotographic copying paper or a planographic plate having an photoconductive image-forming layer of excellent water and organic solvent resistance, coat surface strength and which is excellent in the permanency and printing durability.

In general, it is known that oxygen or water forms a chemical adsorption layer on the surface of supports such as paper. The adsorption is in the nature of a monomolecular film and possesses very strong chemical adhesion.

The chromium atom, in general, combines with water to form a structure of the formula

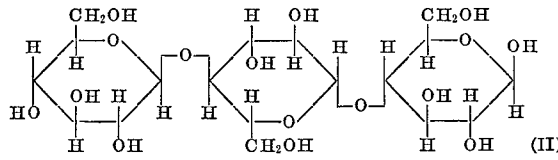


(I)

In accordance with this invention, in order to strongly bond together the support and the photoconductive image-forming layer in an electrophotographic sensitive material,

advantage is taken of both the above-mentioned adsorption layer and the ready formation of a chelate between chromium atoms and water molecules, as well as the further strengthening of the bond resulting from the use of a resin containing OH-groups.

As is well known, cellulose has the structure of the following formula



(II)

and easily absorbs moisture from the air. The —OH groups of the cellulose and chromium atoms react to form a chelate bond and such atoms also react easily with OH-groups and adsorbed water in the image-forming layer, resulting in a very strong bond between the two.

When chromium atoms are partially bonded with a synthetic resin having OH-groups to form a structure similar to triphenyl chromiumtri(tetrahydrofuran) obtained by the reaction of chromium chloride and phenyl magnesium bromide in tetrahydrofuran solvent, the atoms form strong chelate bonds with OH-groups of cellulose or the monomolecular layer or adsorbed water molecules on the surface of a support such as paper, resulting in increased bonding power. They also partially bond with the —OH groups of other pigments or resin molecules or absorbed water, for example, —OH groups on the surface of zinc oxide or titanium dioxide fine powders in the image-forming layer, in a layer of water absorbed in forming the photoconductive image-forming layer or with —OH groups of the adhesive resin to form bridges resulting in a larger cross linking density. This invention is of particular significance in that the support, such as paper, and the photoconductive image-forming layer can be strongly bonded together through the reaction product of a chromium compound and a synthetic resin having —OH groups as an intermediate layer.

As chromium compounds to be used in this invention, there may be mentioned chromous chloride, chromic chloride, chromous nitrate and chromic sulfate. As synthetic resins containing —OH groups, there may be mentioned epoxy, phenol, resorcinol, xylene and butyral resins. The reaction proportions of these materials is preferably 10–25 parts by weight of the chromium compound to 100 parts by weight of the resin.

To promote the smooth reaction of said chromium compound with said synthetic resin, a promoter consisting of a mixture of iodine, metallic magnesium and either tetrahydrofuran, pyridine or melamine is added to the reaction system. The amount of promoter used is suitably about 200–300 parts by weight of tetrahydrofuran, pyridine or melamine, 10–30 parts by weight of iodine and 3–6 parts by weight of metallic magnesium, to each 100 parts by weight of resin.

The reaction temperature employed may range from about 70–80° C.

As supports, there may be employed a wood-free paper or a paper which has been subjected to a resistance lowering treatment with a high molecular weight electrolyte, such as a quaternary ammonium salt, so that its resistance is below 10^{10} Ω-cm., art paper, plastic sheet, thin metallic film, for example, aluminum foil and the like. These supports may be, if necessary, coated with a water soluble resin such as methyl cellulose, polyvinyl alcohol, starch, casein and the like for use.

As compounds to be employed in the photoconductive image-forming layer, conventionally known substances may be employed. For example, there may be employed photoconductive fine powders, such as zinc oxide, titanium

dioxide, zinc sulfide, cadmium sulfide, lead oxide and the like; as sensitizers, there may be employed Rose Bengale, uranine, Eosine, Malachite Green, Auramine, Crystal Violet, Lewis acids and the like. As resin bonding agents there may be used silicone resins, acrylic resins, alkyd resins, polyester resins, vinyl acetate resins, a vinyl acetate-acrylic acid ester copolymer, an ethylene-vinyl acetate copolymer and the like.

Other than such compositions consisting of a photoconductive fine powder, sensitizer and resin binder, photoconductive resins have also been used recently in such image-forming layers. In the composition of the present invention, there may likewise be employed as such a photoconductive resin, such materials as polyvinyl carbazole, polyvinyl acridine, polyvinyl triphenyl pyrazoline and the like in the image-forming layer.

The accompanying drawing shows a section view of an electrophotographic sensitive material according to this invention, in which **1** is the support, **2** is an intermediate layer of the reaction product of a chromium compound with a resin containing —OH groups and **3** is a photoconductive image-forming layer.

This invention will be illustrated more fully by the following examples.

EXAMPLE 1

100 g. of epoxy resin (Epicoat #834 manufactured by Shell Oil Co.) is dissolved in 700 g. of n-butyl acetate with heating and 25 g. of iodine is incrementally added thereto. After stirring 2 hrs. at 70° C., 300 g. of purified tetrahydrofuran and then 5 g. of metallic magnesium chips are added and dissolved with reaction. 15 g. of chromic chloride ($CrCl_3$) in the form of a dried powder is then incrementally added and stirred at 70° C. for 4 hours to react them. The precipitate is removed, washed with water and dried with anhydrous sodium sulfate. After filtration, a mixed solvent of toluene, ethylene glycol monobutyl ether and methyl isobutyl ketone (1:1:1 in weight ratio) is added to yield a transparent dark green solution containing 30 wt. percent of non-volatile matter. The thus obtained reaction product is coated on a support of wood-free paper weighing 50 g./m.^{2} and dried at 100° C. for 30 sec. to form three intermediate layers having weights of 2 g./m.^{2}, 4 g./m.^{2} and 8 g./m.^{2}, respectively.

A paint consisting of 100 g. of photoconductive zinc oxide (Franch Method), 40 g. of silicon resin (KR–211 manufactured by Shinetsu Chemical Co.) containing 70 wt. percent of non-volatile matter, 4 ml. of a solution of 1 g. of Rose Bengale dissolved in 100 ml. of methanol and 100 g. of toluene is coated on each of the above respective intermediate layers and dried at 100° C. for 20 sec. to form image-forming layers having a coat weight of 20 g./m.^{2}, to obtain electrophotographic sensitive materials.

These materials are used as planographic plates, images being formed on the image-forming layers by a conventional electrophotographic process and tested on an offset printing machine (A. B. Dick 350-Type Printing Machine manufactured by A. B. Dick Co., England). Excellent printing durability was obtained, as shown in Table 1.

Sample No.	Composition of intermediate layer	Coating weight of intermediate layer (g./m.^{2})	No of sheets printed
A	Reaction product of Cr compound and epoxy resin.	2	2,600
B	do	4	5,500
C	do	8	7,000
D	Epoxy resin [1]	8	300

[1] Epicoat 834.

Sample D in the above Table 1 has an intermediate layer of epoxy resin and is a planographic plate formed under the same conditions as Samples A, B and C.

Epoxy resins are, in general, thermo-setting. However, the setting occurs only slightly under drying conditions of 100° C. for 30 sec., as seen from the results obtained with Sample D. Thus, the intermediate layers of Samples A, B and C, comprising a reaction product obtained by reacting epoxy resin and chromium compound, are not dissolved in toluene, whereas the intermediate layer of Sample D is readily dissolved in toluene.

However, the primary importance of this invention consists not in the insolubility of the intermediate layer, but rather in the strengthening of the adhesion between the support and the image-forming layer, as mentioned above. In fact, Samples A, B and C show extremely larger resistance in bending separation as compared with Sample D.

The same results are obtained when, instead of high quality paper as used in Example 1, there is used a high quality paper, the surface of which has been coated lightly with starch, a commercial art paper or aluminum foil-paper as the support. The above electrophotographic sensitive material may also be used as is as an electrophotographic copying paper.

EXAMPLE 2

100 g. of phenol resin (Super Beckasite 1001, manufactured by Dai-Nippon Ink Chemical Industry Co.) is dissolved in 500 g. of a mixed solvent of toluene and butanol (weight ratio: 1:1) with heating and 20 g. of iodine is added incrementally thereto. After stirring at 80° C. for 3 hours, 200 g. of purified pyridine is added and 4 g. of metallic magnesium chips is added and dissolved with reaction. 15 g. of chromic chloride ($CrCl_3$) in the form of dried powder is incrementally added and stirred at 80° C. for five hours. The resulting precipitate is removed, washed with water and dried with anhydrous sodium sulfate and, after filtration, a mixed solvent of xylene and ethylene glycol monobutyl ether in a weight ratio of 1:1 is added to yield a transparent dark green solution containing 30 wt. percent non-volatile matter.

The thus obtained reaction product is coated on a support of wood-free paper and dried at 100° C. for 30 sec. to form an intermediate layer having a coat weight of 5 g./m.^{2}. A paint consisting of 100 g. of finely divided photoconductive zinc oxide, 50 g. of acrylic resin containing 40 wt. percent non-volatile matter (OD–A–111–40 manufactured by Dai-Nippon Ink Chemical Co.), 4 ml. of a solution of 1 g. of Rose Bengale in 100 ml. of methanol and 100 g. of toluene is coated on the intermediate layer and dried at 100° C. for 20 sec. to yield an electrophotographic sensitive material having an image-forming layer having a coat weight of 20 g./m.^{2}.

This material is used as a planographic plate to form an image and subjected to a printing test by means of an off-set printing machine resulting in a printing durability of more than 7,000 sheets.

EXAMPLE 3

100 g. of finely divided titanium dioxide of the rutile type and 50 g. of methyl ethyl ketone are added to 100 g. of the reaction product obtained in Example 2 containing 30 wt. percent non-volatile matter and treated in a ball mill to form a paint, which is coated on a support of wood-free paper and dried at 100° C. for 20 sec. to form an intermediate layer having a coated weight of 15 g./m.^{2}. An image-forming layer having the same composition and coating weight as in Example 1 is formed on the intermediate layer to yield an electrophotographic sensitive material.

This material is used as a planographic plate to form an image and subjected to a printing test by means of an off-set printing machine resulting a printing durability more than 8,000 sheets.

EXAMPLE 4

Following the procedure of Example 1, an intermediate layer is formed to yield an electrophotographic sensitive material using the following components. The result obtained is similar to that in Example 1.

	G.
Resorcinol resin (Aichibond R manufactured by Aichi Chemical Co.)	100
Xylene/ethyl acetate (1:1)	800
Iodine	25
Tetrahydrofuran	300
Metallic magnesium	5
Chromous nitrate	15

Following the procedure of Example 1, but substituting the components as shown below in Examples 5 to 9 for the intermediate layer, substantially identical results were obtained.

EXAMPLE 5

	G.
Vinyl butyral resin of 11%-OH content (Eslex BL-1 manufactured by Sekisui Chemical Co.)	100
Ethyl acetate/butanol (1:1)	750
Iodine	20
Tetrahydrofuran	200
Metallic magnesium	5
Chromous chloride ($CrCl_2$)	20

EXAMPLE 6

Vinyl butyral resin of 19%-OH content	100
Dioxane/butanol (1:1)	800
Iodine	15
Pyridine	200
Metallic magnesium	5
Chromic sulfate ($Cr_2(SO_4)_3$)	15

EXAMPLE 7

Epoxy resin of Example 1/phenol resin of Example 2 (1:1)	100
Toluene/methyl ethyl ketone (1:1)	800
Iodine	15
Tetrahydrofuran	150
Metallic magnesium	5
Chromic chloride	15

EXAMPLE 8

Phenol resin of Example 2/resorcinol resin of Example 4 (2:1)	100
Xylene/butanol (1:1)	700
Iodine	15
Melamine	200
Metallic magnesium	5
Chromic chloride	15

EXAMPLE 9

Xylene resin (Xylenetex manufactured by Oriental Paint Co.)	100
Xylene/ethyl acetate (1:1)	800
Iodine	20
Pyridine	200
Metallic magnesium	5
Chromic nitrate	15

The picking strength of off-set master paper from the electrophotographic materials of Examples 1–9 is 8A or more. However, the picking strength of photoconductive image-forming layer on a support without an intermediate layer is less than 2A and those in which epoxy resin is used in the intermediate layer show a strength of less than 4A. From these facts, the advantages of the present invention will be readily apparent.

As is obvious from the examples, the formation of the intermediate layer of the reaction product of a chromium compound and a synthetic resin containing —OH groups very strongly bonds the image-forming layer to a support such as paper and the resulting sensitive material possesses particular utility as copying paper, especially in wet development systems and is suitable for maps. It provides, when used as a planographic plate, a good printing durability which has never before been obtained.

What is claimed is:

1. A process for the manufacture of an electrophotographic sensitive element, which comprises:
   (a) reacting at least one resin, containing —OH groups selected from the group consisting of an epoxy resin, a phenol resin, a resorcinol resin, a xylene resin and a butyral resin, with a chromium compound selected from the group consisting of chromous chloride, chromic chloride, chromous nitrate, and chromic sulphate, to yield a paint,
   (b) coating the paint on a support,
   (c) drying, and
   (d) coating thereon, a photo conductive image-forming layer comprising a resinous component,
   the reaction proportions of the afore-mentioned materials being present in an amount of from 10 to 25 parts by weight of said chromium compound to 100 parts by weight of said resin, and the said reaction being carried out at a temperature of from 70–80° C.

2. The process of claim 1 wherein said reaction is carried out in the presence of a promoter comprising iodine, metallic magnesium, and a member selected from the group consisting of tetrahydrofuran, pyridine and melamine, said member being present in an amount of from 200 to 300 parts by weight, said iodine being present in an amount of 10 to 30 parts by weight, and said metallic magnesium being present in an amount of 3 to 6 parts by weight for each 100 parts by weight of said resin.

3. The process of claim 1 wherein said photoconductive image-forming layer contains a photoconductive powder selected from the group consisting of zinc oxide, titanium dioxide, zinc sulfite, cadmium sulfite and lead oxide.

4. The process of claim 1, wherein said photoconductive image-forming layer contains as a sensitizer, a member selected from the group consisting of Rose Bengale, uranine, Eosine, Malachite Green, Auramine, Crystal Violet, and Lewis acids.

5. A process for the manufacture of an electrophotographic sensitive element which comprises:
   (a) reacting 100 parts by weight of a resin containing —OH groups selected from the group consisting of an epoxy resin, a phenol resin, a resorsinol resin, a xylene resin, and a butyral resin, with 10 to 20 parts by weight of a chromium compound selected from the group consisting of chromous chloride, chromic chloride, chromous nitrate and chromic sulphate, in the presence of a promoter comprising 10 to 30 parts by weight of iodine, 3 to 6 parts by weight of metallic magnesium, and 200 to 300 parts by weight of a member selected from the group consisting of tetrahydrofuran, pyridine and melamine, said process being carried out at a temperature ranging from 70–80° C. to yield a paint,
   (b) coating the paint on a support,
   (c) drying, and
   (d) coating thereon, a photoconductive image-forming layer comprising a resinous component.

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96—1.5, 1.6, 1.7; 117—34, 218 138.8 PU, 138.8 A, 132 BE, 76 P; 101—457, 462