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(54) A method for manufacturing an electrophotographic organic photoconductor.

(57) A method for manufacturing an electrophotographic organic photoconductor is disclosed which comprises the steps of forming on the surface of a conductive base a charge transport layer consisting of a first resin composition and forming on the surface of the charge transport layer a charge generating layer consisting of a second resin composition. In this method, the step of forming the charge transport layer includes the application of a charge transport layer coating solution containing the first resin composition and a solvent onto the surface of the conductive base for the formation of a layer of the coating solution and the heat treatment of the coating solution layer at a temperature higher than the glass-transition temperature (Tg) of the first resin composition and lower than the melt-starting temperature of the first resin composition.

A METHOD FOR MANUFACTURING AN ELECTROPHOTOGRAPHIC ORGANIC PHOTOCONDUCTOR

The present invention relates to a method for manufacturing an electrophotographic organic photoconductor having an organic photoconductive layer. More particularly, the invention relates to a method for manufacturing a multilayer-structured electrophotographic organic photoconductor, including the steps of forming a charge transport layer on the surface of a conductive base, forming a charge generating layer on the surface of the charge transport layer, and forming a surface protective layer on the surface of the charge generating layer.

Multilayer-structured electrophotographic organic photoconductors are usually manufactured in the following manner.

First, a charge transport layer coating solution containing a resin composition and a solvent is applied onto the surface of a conductive base, which is heated and dried to form a charge transport layer. Then, a charge generating layer coating solution containing a resin composition and a solvent is applied onto the surface of the charge transport layer, which is heated and dried to form a charge generating layer. Next, a surface protective layer coating solution containing a resin composition and a solvent is applied onto the surface of the charge generating layer, which is heated and dried to form a surface protective layer.

The heating process for each of the above layers is performed not only to vaporize the solvent contained in each coating solution but also to provide each layer with intended properties. If the conditions of heat treatment employed in the heating process are inadequate, the properties of the produced photoconductor such as sensitivity and repeatability will deteriorate. Furthermore, the surface hardness of the surface protective layer will also drop. It is therefore required that each layer be adequately heated.

To determine the heating conditions (heating temperature and heating time) for each layer, there has previously been employed a method wherein each layer is actually heated under various different conditions and the properties of each of the thus produced photoconductors are measured to find out the desirable conditions of heat treatment. In other words, the conditions of heat treatment for each layer have been determined by trial and error. The previous method therefore has had a disadvantage in terms of production efficiency since any change in the formulation of each layer requires separate determination of the heat treating temperature. Another problem with the previous method has been the inability to determine the optimum conditions of heat treatment.

In particular, the conditions of heat treatment for the surface protective layer have been determined mainly by actually measuring the relationship between the heat treating time and the pencil hardness of the surface protective layer in the following manner. Heat treatment accelerates the crosslinking in the resin composition forming the surface protective layer, and it is believed there is a correlation between the crosslinking degree and the hardness of the surface protective layer. Therefore, in the previous method, it has been judged, on the basis of the predetermined correlation between the heat treating time and the pencil hardness of the surface protective layer, that sufficient heat treatment is done at the point of time when a prescribed pencil hardness is obtained.

However, even when the heat treatment has been performed for a time required for attaining the pencil hardness of the surface protective layer, there have been some cases in which desired properties (sensitivity and repeatability) of the photoconductor cannot be obtained. Therefore, to obtain a photoconductor having excellent properties, it is necessary to measure the relationships of the heat treating time not only with respect to the pencil hardness but also with respect to the sensitivity and to the repeatability. However, such a method involves laborious work and presents a problem in terms of production efficiency.

Incidentally, as the solvent used in the charge generating layer coating solution, a solvent that hardly dissolves the charge transport layer is used. However, when a substance of high crystallinity such as ethyl carbazole hydrazone or such as having a butadiene structure is used as a charge transport substance to be contained in the charge transport layer, the phenomenon is noted that fine, elongated cracks are caused in numerous numbers in the charge transport layer when the charge generating layer coat ing solution is applied on the surface of the charge transport layer.

This phenomenon is considered attributable to the following cause. Since the crystallinity of the charge transport substance is very high, the charge transport layer is formed with internal strain contained. When the charge generating layer coating solution is applied on the surface of the charge transport layer a small amount of the charge transport substance is dissolved by the solution although the resin in the charge transport layer is not dissolved. As the charge transport substance is dissolved by the solution, the internal strain in the charge transport layer is released, and the resulting energy acts to cause the cracks.

The method for manufacturing an electrophotographic organic photoconductor of this invention, which overcomes the above-discussed and numerous other disadvantages and deficiencies of the prior art, comprises the steps of: forming on the surface of a conductive base a charge transport layer consisting of a first resin composition; and forming on the surface of the charge transport layer a charge generating layer consisting of a second resin composition, wherein the step of forming the charge transport layer includes: the application of a charge transport layer coating solution containing the first resin composition and a solvent onto the surface of the conductive base for the formation of a layer of the coating solution; and the heat treatment of the coating solution layer at a temperature higher than the glass-transition temperature (Tg) of the first resin composition and lower than the melt-starting temperature of the first resin composition.

In a preferred embodiment, the method for manufacturing an electrophotographic organic photoconductor comprises the steps of: forming on the surface of a conductive base a charge transport layer consisting of a first resin composition; and forming on the surface of the charge transport layer a charge generating layer consisting of a second resin composition, wherein the step of forming the charge generating layer includes: the application of a charge generating layer coating solution containing the second resin composition and a solvent onto the surface of the charge transport layer for the formation of a layer of the coating solution; and the heat treatment of the coating solution layer at a temperature lower than the melt-starting temperature of the first resin composition.

In a preferred embodiment, the method for manufacturing an electrophotographic organic photoconductor comprises the steps of: forming on the surface of a conductive base a charge transport layer consisting of a first resin composition; forming on the surface of the charge transport layer a charge generating layer consisting of a second resin composition; and forming on the surface of the charge generating layer a surface protective layer consisting of a third resin composition, wherein the step of forming the surface protective layer includes: the application of a surface protective layer coating solution containing the third resin composition and a solvent onto the surface of the charge generating layer for the formation of a layer of the coating solution; and the heat treatment of the coating solution layer at a temperature lower than the melt-starting temperature of the charge transport layer consisting of the first resin composition.

In a preferred embodiment, the method for manufacturing an electrophotographic organic photoconductor comprises the step of forming a resin layer on the surface of a conductive base, wherein the step includes the application of a coating solution containing a solvent and a binding resin made of a thermosetting resin and the drying of a layer of the coating solution under prescribed conditions, the prescribed drying conditions being determined by examining the reduction of a reactive group present in the thermosetting resin by means of infrared absorption spectroscopy.

In a preferred embodiment, the above-mentioned thermosetting resin is a silicone resin having a silicone oligomer as the main component.

In a more preferred embodiment, the method for manufacturing an electrophotographic organic photoconductor comprises the steps of: forming on the surface of a conductive base a charge transport layer consisting of a first resin composition; and forming on the surface of the charge transport layer a charge generating layer consisting of a second resin composition, wherein the step of forming the charge generating layer includes the application and drying of a charge generating layer coating solution containing the second resin composition and a solvent onto the surface of the charge transport layer while holding the base with the charge transport layer formed thereon at a temperature within the range of 33° C to the glass-transition temperature (Tg) of the first resin composition.

Thus, the invention described herein makes possible the objectives of:

(1) providing a method for manufacturing an electrophotographic organic photoconductor, wherein the conditions of heat treatment for the charge transport, charge generating, and surface protective layers can be determined in a simple process;

(2) providing a method capable of manufacturing an electrophotographic organic photoconductor having stable properties including sensitivity and repeatability;

(3) providing a method for manufacturing an electrophotographic organic photoconductor also having excellent surface smoothness;

(4) providing a method for manufacturing an electrophotographic organic photoconductor, wherein there is no possibility of cracks being caused in the charge transport layer even when a charge transport substance with high crystallinity is used; and

(5) providing a method for manufacturing an electrophtographic organic photoconductor, capable of enhancing production efficiency.

In the description which follows, reference will be made to the accompanying drawings, wherein:

Figures 1 to 3 are graphs showing the relationships of the heat treating time with respect to the ratio of the absorption peak (3400 cm^{-1}) of a hydroxyl group (-OH) to the absorption peak (2900 cm^{-1}) of a methyl group ($-CH_3$).

Figure 4 is a graph showing the relationship between the heat treating time and the pencil hardness of the surface protective layer.

Figure 5 is a graph showing the relationship between the heat treating time and the half-value exposure 1/2 (Lux•Sec).

The present invention is applicable to a method for manufacturing various multilayer-structured electrophotographic organic photoconductors. In particular, the present invention is applicable to a method for manufacturing a photoconductor having a conductive base, a charge transport layer formed on the surface of the conductive base, a charge generating layer formed on the surface of the charge transport layer, and a surface protective layer formed on the surface of the charge generating layer.

Formation of the charge transport layer:

To form the charge transport layer, a charge transport layer coating solution containing a first resin composition and a solvent is first applied onto the surface of the conductive base, and then, the coating solution layer is heated and dried at a prescribed temperature. The first resin composition contains a binding resin, a charge transport substance, etc.

According to the present invention, the heat treating temperature for the coating solution layer should be within the range of temperatures higher than the glass-transition temperature (Tg) of the first resin composition and lower than the melt-starting temperature of the first resin composition, preferably within the range of temperatures at least 10° C higher than the glass-transition temperature (Tg) of the first resin composition and at least 10° C lower than the melt-starting temperature of the first resin composition.

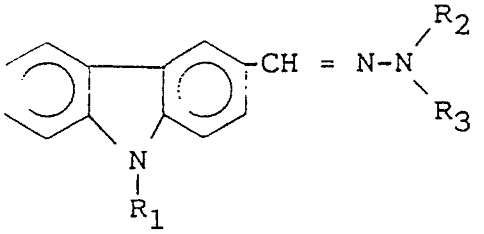
If the heat treating temperature is lower than the glass-transition temperature (Tg) of the first resin composition, internal strain tends to remain in the charge transport layer. This will cause irregularities on the surface of the charge transport layer when a charge generating layer coating solution containing a second resin composition and a solvent is applied on the surface of the charge transport layer. Conversely if the heat treating temperature is higher than the melt-starting temperature of the first resin composition, the formed charge transport layer will melt and deform under its own weight, damaging the surface smoothness of the charge transport layer.

Heat treatment is performed by storing the conductive base with the coating solution layer formed thereon in a drying oven equipped, for example, with a hot water circulator, a steam circulator, an infrared or tungsten heater, etc. The heat treating time is suitably adjusted in accordance with the formulation of the coating solution, the thickness of the coating solution layer, the heating capacity of the heating oven, etc. The glass-transition temperature (Tg) and melt-starting temperature of the first resin composition are obtained by actually measuring them. The actual measurement of these temperatures can be accomplished either by actually forming a charge transport layer on the surface of the conductive base and examining the thus prepared conductive base or by making a test piece having the same construction as that of the photoconductor and examining the charge transport layer formed on the test piece.

As the binding resin contained in the first resin composition, a prior known resin is used. Examples include styrene type polymer, styrene-butadiene copolymer, styrene-acrylonitrile copolymer, styrene-maleic acid copolymer, acrylic copolymer, styrene-acrylate copolymer, ethylene-vinyl acetate copolymer, polyvinyl chloride, vinyl chloride-vinyl acetate copolymer, polyester, alkyd resin, polyamide, polyurethane, acrylic modified urethane resin, epoxy resin, polycarbonate, polyarylate, polysulfone, diallylphthalate resin, silicone resin, ketone resin, polyvinyl butyral resin, polyether resin, phenol resin and the like.

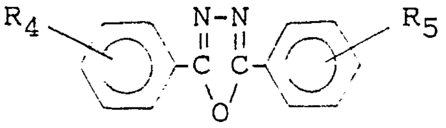
As the above-mentioned solvent, a known solvent capable of dissolving the binding resin is used.

As the above-mentioned charge transport substance, a substance with high crystallinity is generally used. For example, its general formula may be represented by one of the following formulae (1) to (4).



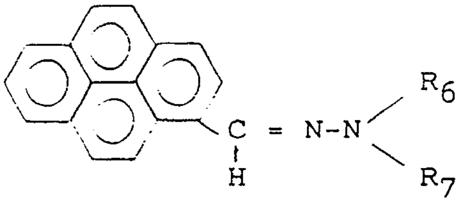
...(1)

(In the formula, an alkyl group or alkoxy group is denoted by **R**$_1$. **R**$_2$ and **R**$_3$ are independently hydrogen, a nitro group, an alkyl group, an alkoxy group, a substituted or non-substituted phenyl group, a benzyl group, a group having an indole ring, an N-alkylcarbazolyl group, a fluorenoyl group, or a triphenylallyl group.)



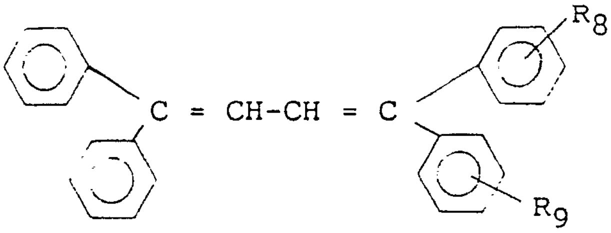
...(2)

[In the formula, R_4 and R_5 are independently a substituted amino group (its substituent is an alkyl group, an alkoxy group, halogen, or a nitro group), hydrogen, a nitro group, an alkyl group, an alkoxy group, a substituted or non-substituted phenyl group a benzyl group, a group having an indole ring, an N-alkylcarbazolyl group, a fluorenoyl group, or a triphenylallyl group.]



...(3)

(In the formula, **R6** or **R7** are independently hydrogen, a nitro group, an alkyl group, an alkoxy group, a substituted or non-substituted phenyl group, a benzyl group, a group having an indole ring, an N-alkylcarbazolyl group, a fluorenoyl group, or a triphenylallyl group.)



...(4)

[In the formula, **R8** and **R9** are independently a substituted amino group (its substituent is an alkyl group, an alkoxy group, halogen or a nitro group), hydrogen, a nitro group, an alkyl group, an alkoxy group, a substituted or non-substituted phenyl group, a benzyl group, a group having an indole ring, an N-alkylcarbazolyl group, a fluorenoyl group, or a triphenylallyl group.]

Formation of the charge generating layer:

To form the charge generating layer, a charge generating layer coating solution containing a second resin composition and a solvent is first applied onto the surface of the charge transport layer, and then, the coating solution layer is heated and dried at a prescribed temperature. The second resin composition contains a charge generating substance, a binding resin, etc.

It is desirable that the charge generating layer coating solution be applied onto the surface of the charge transport layer with the conductive base having the charge transport layer formed thereon kept at a temperature within the range of 33° C to the glass-transition temperature (Tg) of the first resin composition. By keeping the surface of the charge transport layer in such heated condition, the internal residual strain in the charge transport layer can be released. Therefore, even if the charge transport substance contained in the charge transport layer is dissolved by the charge generating layer coating solution there occurs no energy great enough to cause cracks in the charge transport layer. If the temperature of the charge transport layer is lower than 33° C when applying the charge generating layer coating solution, cracks tend to be caused in the charge transport layer when the charge generating layer coating solution is applied.

Conversely, if the temperature of the charge transport layer is higher than the glass-transition temperature (Tg) of the charge transport layer when applying the charge generating layer coating solution, irregularities tend to be caused on the surface of the charge generating layer.

The heat treating temperature for the charge generating coating layer applied on the surface of the charge transport layer should be lower than the melt-starting temperature of the first resin composition, preferably at least 5 °C lower than the melt-starting temperature of the first resin composition. If the heat treating temperature is higher than the melt-starting temperature of the first resin composition, the charge transport layer will melt and deform under its own weight, thus damaging the surface smoothness of the charge generating layer.

As the binding resin contained in the second resin composition, the same one as used in the first resin composition can be used. A substance capable of dissolving the binding resin is used as the solvent, while a known substance is used as the charge generating substance.

Formation of the surface protective layer:

To form the surface protective layer, a surface protective layer coating solution containing a third resin composition and a solvent is first applied on the surface of the charge generating surface, and then, the coating solution layer is heated and dried at a prescribed temperature. The third resin composition contains a binding resin or the like.

The heat treating temperature for the coating solution layer should be lower than the melt-starting temperature of the first resin composition, preferably at least 5 °C lower than the melt-starting temperature of the first resin composition. If the heat treating temperature is higher than the melt-starting temperature of the first resin composition, the charge transport layer will melt and deform under its own weight, thus damaging the surface smoothness of the surface protective layer.

As the binding resin contained in the third resin composition, the same one as used in the first resin composition can be used. A substance capable of dissolving the binding resin is used as the solvent.

Thus, by measuring the glass-transition temperature and melt-starting temperature of the first resin composition, it is possible to know the desirable heat treating temperatures for forming the charge transport layer, the charge generating layer, and the surface protective layer. Furthermore, by keeping the temperature of the charge transport layer at a pre scribed temperature when applying the charge generating layer coating solution, a photoconductor having a good surface condition can be produced without causing cracks in the charge transport layer. This allows the use of a charge transport substance having high crystallinity, and therefore, provides a wider selection of materials for use as the charge transport substance.

If a thermosetting resin is used in the binding resin contained in each of the charge transport layer, charge generating layer, and surface protective layer coating solutions, the conditions of heat treatment for each applied solution layer can be determined in the following manner.

The reduction of a reactive group present in the thermosetting resin contained in each solution layer is measured by infrared absorption spectroscopy. The conditions of heat treatment under which there occurs no further reduction of the reactive group or the reactive group is reduced to the minimum in the course of heating is determined as the optimum conditions of heat treatment for that layer. The measurement can be made either by actually producing a photoconductor and examining each layer formed thereon or by making a test piece having the same construction as that of the photoconductor and examining each layer formed on the test piece.

It is desirable that the reduction of the reactive group be measured by comparing the infrared absorption spectrum of the reactive group present in the thermosetting resin with that of a group different from the reactive group (a group detectable by infrared absorption spectroscopy). As a group different from the reactive group present in the thermosetting resin a group whose infrared absorption spectrum does not vary by heating, for example, an alkyl group such as a methyl group, is preferably used.

As the thermosetting resin, any of the resins conventionally used in the coating solutions can be used. Examples include silicone resin, polyester, alkyd resin, polyamide, polyurethane, acrylic modified urethane resin, epoxy resin, polycarbonate, polyarylate, polysulfone, diallyl phthalate resin, ketone resin, polyvinyl butyral resin, polyether resin, phenol resin or the like. As the substituent group, a hydroxyl group, a carboxyl group, an amino group, an isocyanate group, an epoxy group or the like. A combination of two or more thermosetting resins may be used. In that case, it is desirable that the above measurement be made with respect to the resin that needs the longest heat treating time.

The following description deals with one example of a method for determining the optimum conditions of heat treatment for the surface protective layer which is formed using a silicone resin as the thermosetting resin with a silicone oligomer as the main component.

Since the silicone resin uses trifunctional alkylsilane as the starting material, it contains a silanol group (-SiOH). Through dehydration and polymerization by heating, the silanol group turns into -SiOSi-, reducing the infrared absorption of the hydroxyl group (-OH). The infrared absorption of the alkyl group (for example, a methyl group ($-CH_3$)) present in the silicone resin does not vary by heating.

Therefore, the infrared absorption spectrum of the surface protective layer is measured to obtain the ratio of the absorption peak (3400 cm^{-1}) of the hydroxyl group (-OH) to the absorption peak (2900 cm^{-1}) of the methyl group ($-CH_3$). Change in the ratio is observed with respect to the time, and the time at which the ratio becomes nearly constant is determined as the completion time of the heat treatment.

According to the above method, the optimum conditions of heat treatment for each layer can be determined in a short period of time. By using the RAS method of FT-IR, the above method can be used to inspect the finished product.

The following examples illustrate this invention:

Example 1

A charge transport layer coating solution was prepared by mixing 100 parts by weight of polyarylate (manufactured by Unichika, Trade name: U-100), 100 parts by weight of 4-(N,N-diethylamino) benzaldehyde-N,N-diphenylhydrazone (manufactured by Kurita Kagaku Kenkyusho), and 900 parts by weight of methylene chloride (CH_2Cl_2). After applying the thus prepared coating solution on the surface of an aluminum drum of 78 mm outer diameter and 340 mm in length, the coating solution layer was dried by heating at each of the temperatures prescribed in Table 1 for 30 minutes, to form a charge transport layer of 20 µm thickness (Sample Nos. 1 to 8). The glass-transition temperature (Tg) of the charge transport layer was 58°C, and the melt-starting temperature thereof was 115°C.

The coating film condition of the charge transport layer was examined, the results of which are shown in Table 1. From the results shown in Table 1, it was confirmed that a good coating film can be obtained when the charge transport layer is heat-treated at a temperature higher than the glass-transition temperature (Tg) of the charge transport layer and lower than the melt-starting temperature thereof.

Example 2

A charge generating layer coating solution was prepared by mixing 80 parts by weight of 2,7-dibromoanthanthrone (manufactured by ICI), 20 parts by weight of metalfree phthalocyanine (manufactured by BASF), 50 parts by weight of polyvinyl acetate (manufactured by Nippon Gosei Kagaku, Trade name: Y5-N), and 2000 parts by weight of diacetone alcohol. Then, after applying the thus prepared coating solution on top of the charge transport layer (Sample No. 5) which was formed in Example 1 at a heat treating temperature of 100°C, the coating solution layer was dried by heating at each of the temperatures prescribed in Table 2 for 30 minutes, to form a charge generating layer of 0.5 µm thickness (Sample Nos. 9 to 13).

The coating film condition of the charge generating layer was examined, the results of which are shown in Table 2. From the results of Table 2 it was confirmed that a good coating film can be obtained when the charge generating layer is formed at a temperature lower than the melt-starting temperature of the charge transport layer.

Example 3

A liquid mixture was first prepared by mixing 57.4 parts by weight of 0.02N hydrochloric acid and 86 parts by weight of isopropyl alcohol, and then, while stirring the mixture with its temperature kept at 20 to 25°C, 80 parts by weight of methyltrimethoxysilane and 20 parts by weight of glycidoxypropyltrimethoxysilane were gradually dripped into the mixture. The mixture was then left at room temperature for one hour to obtain a silane hydrolyzate solution.

A surface protective layer coating solution was prepared by adding to the silane hydrolyzate solution 10 parts by weight of polyvinyl acetate having an average polymerization degree of 2000, 20 parts by weight of acetic acid, 0.5 parts by weight of triethylamine as a curing agent, 50 parts by weight of fine powder of antimony doped tin oxide (manufactured by Sumitomo Cement) as a conductive additive, and 0.3 parts by weight of a silicone type surfactant.

After applying the coating solution on top of the charge generating layer (Sample No. 10) which was formed in Example 2 at a heat treating temperature of 110 °C, the coating solution layer was dried by heating at each of the temperatures prescribed in Table 3 for 30 minutes, to form a surface protective layer of 2.5 µm thickness (Sample Nos. 14 to 18).

The coating film condition of the charge generating layer was examined, the results of which are shown in Table 3. From the results shown in Table 3, it was confirmed that a good coating film can be obtained when the surface protective layer is formed at a temperature lower than the melt-starting temperature of the charge transport layer.

Table 1

Sample No.	Heat treating temperature of Charge transport layer (°C)	Coating film condition
1	55	Irregularities are caused after applying the charge generating coating solution
2	70	good
3	80	good
4	90	good
5	100	good
6	105	good
7	120	Irregularities on the surface are caused while heat treating
8	130	Irregularities on the surface are caused while heat treating

Table 2

Sample No.	Heat treating temperature of charge generating layer (° C)	Coating film condition
9	100	good
10	110	good
11	115	good
12	118	Irregularities are caused on the charge transport layer
13	125	Irregularities are caused on the charge transport layer

Table 3

Sample No.	Heat treating temperature of the surface protective layer (°C)	Coating film condition
14	100	good
15	110	good
16	115	good
17	118	Irregularities are caused on the charge transport layer
18	125	Irregularities are caused on the charge transport layer

Example 4

A charge transport layer coating solution was prepared by mixing 100 parts by weight of polyarylate (manufactured by Unichika, Trade name: U-100), 100 parts by weight of 4-(N,N-diethylamino) benzaldehide-N,N-diphenylhydrazone, and 900 parts by weight of methylene chloride (CH_2Cl_2). After applying the thus prepared coating solution on the surface of an aluminum drum of 78 mm outer diameter and 340 mm in length, the coating solution layer was dried by heating at 100° C for 30 minutes, to form a charge transport layer of 20 μm thickness.

A charge generating layer coating solution was prepared by mixing 80 parts by weight of 2,7-dibromoanthanthrone (manufactured by ICI), 20 parts by weight of metalfree phthalocyanine (manufactured by BASF), 50 parts by weight of polyvinyl acetate (manufactured by Nihon Gosei Kagaku, Trade name: Y5-N), and 2000 parts by weight of diacetone alcohol. Then, after applying the thus prepared coating solution on top of the charge transport layer, the coating solution layer was dried by heating under the same conditions as those of the above, to form a charge generating layer of 0.5 μm thickness.

A liquid mixture was prepared by mixing 57.4 parts by weight of 0.02N hydrochloric acid and 86 parts by weight of isopropyl alcohol, and then, while stirring the mixture with its temperature kept at 20 to 25° C, 80 parts by weight of methyltrimethoxysilane and 20 parts by weight of glycidoxypropyltrimethoxysilane were gradually dripped into the mixture. The mixture was then left at room temperature for one hour to obtain a silane hydrolyzate solution.

A surface protective layer coating solution was prepared by adding to the silane hydrolyzate solution 10 parts by weight of polyvinyl acetate having an average polymerization degree of 2000, 20 parts by weight of acetic acid, 0.5 parts by weight of triethylamine as a curing agent, 50 parts by weight of fine powder of antimony doped tin oxide (manufactured by Sumitomo Cement) as a conductive additive, and 0.3 parts by weight of a silicone type surfactant. The surface protective layer coating solution was applied on top of the charge generating layer, and cured by heating at 120° C for each of the times prescribed in Table 4, to form a surface protective layer of a silicone resin having a thickness of 2.5 μm. Thus, a drum type electrophotographic organic photoconductor was manufactured having multiple photoconductive layers.

The polyvinyl acetate (average polymerization degree of 2000) used in this example was prepared by a solution polymerization method in which vinyl acetate monomers were diluted with methyl alcohol and azobisisobutyronitrile (AIBN) was used as the polymerization initiator. The adjustment of the average polymerization degree was performed by controlling the amounts of catalyst, solvent, etc.

In the heat treatment of the surface protective layer, the infrared absorption spectrum of the surface protective layer was measured after particular heat treating times to obtain the absorption peak (3400 cm^{-1}) of the hydroxyl group (-OH) and that (2900 cm^{-1}) of the methyl group ($-CH_3$). Then, the ratio of the absorption peak (3400 cm^{-1}) of the hydroxyl group (-OH) to that (2900 cm^{-1}) of the methyl group ($-CH_3$) was calculated, and the relationship of the ratio with respect to the heat treating time was examined. The results are shown in Table 4 and Figure 1.

Example 5

A surface protective layer consisting of a silicone resin was prepared to form a photoconductor in the same manner as in Example 4 except that polyvinyl butyral (manufactured by Denki Kagaku Kogyo, denka butyral 5000A) was used instead of polyvinyl acetate.

In the heat treatment of the surface protective layer, the relationship between the heat treating time and the ratio of the absorption peak (3400 cm^{-1}) of the hydroxyl group (-OH) to that (2900 cm^{-1}) of the methyl group ($-CH_3$) was examined as in Example 4. The results are shown in Table 4 and Figure 2.

Example 6

A surface protective layer consisting of a silicone resin was prepared to form a photoconductor in the same manner as in Example 4 except that a butylated melamine resin (manufactured by Mitsui Cyanamide, Yuban 128) was used instead of polyvinyl acetate.

In the heat treatment of the surface protective layer, the relationship between the heat treating time and the ratio of the absorption peak (3400 cm^{-1}) of the hydroxyl group (-OH) to that (2900 cm^{-1}) of the methyl group ($-CH_3$) was examined as in Example 4. The results are shown in Table 4 and Figure 3.

Comparative Example 1

In forming the surface protective layer in accordance with the same formulation as used in example 4, the relationship between the heat treating time and the pencil hardness of the surface protective layer was examined. The pencil hardness was measured using a pencil hardness tester manufactured by Mita Kogyo. The pencil hardness H was obtained against the heat treating time 5 minutes, 3H against 10 minutes, 4H against 15 minutes, and 5H against 30 minutes. The relationship is shown in Figure 4. As shown in Figure 4, since the pencil hardness reached a stable level after 30 minutes of heat treating time, it was determined that 30 minutes was adequate as the heat treating time.

Next, the sensitivity and repeatability of each of the photoconductors manufactured using different heat treating times in Example 4 and Comparative Example 1 were measured. The sensitivity and repeatability of such photoconductors were measured as follows:

Sensitivity of the photoconductor: The photoconductor was mounted on an electrostatic copying tester (manufactured by Gentec, Gentec Cynthia Model 30M), and the surface of the photoconductor was positively charged to measure the surface potential $V_{1\ s.p.}$(V). Next, the photoconductor under the above charged condition was exposed by a halogen lamp, the exposure light source of the electrostatic copying tester, under the conditions of an exposure intensity of 0.92 W/cm^2 and an exposure time of 60 msec., to obtain the time needed till the surface potential $V_{1\ s.p.}$ is reduced to half, and the half-value exposure 1/2 (Lux•Sec) was calculated. The results are shown in Table 5 and Figure 5.

Repeatability of the photoconductor: The photoconductor was mounted in a copying machine (manufactured by Mita Kogyo, Model DC-111). After producing 500 copies on the copying machine, the surface potential of the photoconductor was measured (the surface potential after repeated exposures to be denoted as $V_{2\ s.p.}$(V)). The difference between the surface potential $V_{1\ s.p.}$ and the surface potential $V_{2\ s.p.}$ was obtained to obtain the surface potential variation Δ V. The results are shown in Table 6.

Table 4

Time (min.)	5	10	15	30	45	60	90	120	135
Example 4	0.736	0.614	——	0.532	——	0.519	0.405	0.402	——
Example 5	0.950	——	0.814	0.751	0.670	0.648	0.643	0.662	——
Example 6	0.735	0.627	——	0.564	——	0.535	0.500	0.447	0.450

Table 5

Heat treating time (min.)	E 1/2 (Lux.Sec)
5	4.7
10	4.4
15	4.2
30	3.8
60	3.4
90	3.4
120	3.4

Table 6

Heat treating time(min.)	Initial setting surface potential [V]	Surface potential after using 500 times [V]	Δ V
30	764	672	-92
60	753	693	-60
90	738	706	-32
120	740	707	-33

From Table 4, it was confirmed that there is a correlation of the ratio of the absorption peak of the hydroxyl group to that of the methyl group obtained by the infrared absorption spectroscopy with respect to the sensitivity and to the repeatability of the photoconductor.

From Figure 1, it can be seen that 90 minutes is the optimum heat treating time of the surface protective layer. On the other hand, from Figure 4, it can be judged that 30 minutes is adequate as the heat treating time for the surface protective layer since the pencil hardness of the surface protective layer reaches a stable value at the heat treating time of 30 minutes. However, Tables 5 and 6 show that the optimum sensitivity and repeatability of the photoconductor can be obtained when the heat treating time is 90 minutes or longer. That is, the photoconductor was not provided with adequate sensitivity and repeatability under the heat treating time of 30 minutes when the pencil hardness reached a stable value. Point (a) in each of Figures 1 to 4 indicates the optimum drying condition.

Example 7

A charge transport layer coating solution was prepared by mixing 100 parts by weight of polyarylate (manufactured by Unitika, Trade name: U-100), 100 parts by weight of 1,1-diphenyl-4,4-di-(diethylamino)-phenyl 1,3-butadiene (with a melting point of 169° C) as a charge transport substance, and 900 parts by weight of methylene chloride (CH_2Cl_2). After applying the thus prepared coating solution on the surface of an aluminum drum of 78 mm outer diameter and 340 mm in length, the coating solution layer was dried by heating at 100° C for 30 minutes, to form a charge transport layer of 20 µm thickness. The glass-transition temperature (Tg) was 74° C.

A charge generating layer coating solution was prepared by mixing 100 parts by weight of 2,7-dibromoanthanthrone (manufactured by ICI), 50 parts by weight of polyvinyl acetate (manufactured by Nihon Gosei Kagaku, Trade name: Y5-N), and 2000 parts by weight of diacetone alcohol.

Next, with the charge transport layer kept at each of the temperatures shown in Table 7, the charge generating layer coating solution was applied onto the surface of the charge transport layer (Sample Nos. 19 to 24). After that, the coating solution layer was dried by heating at 110° C for 30 minutes to form a charge generating layer of 0.5 µm thickness.

The surface condition of the charge generating layer coating solution applied on the surface of the charge transport layer was examined, the results of which are shown in Table 7.

Example 8

A charge transport layer was prepared in the same manner as in Example 7 except that ethyl carbonate diphenylhydorazone (with the melting point of 152° C) was used as a charge transport substance. The glass-transition temperature (Tg) of the charge transport layer was 66° C.

Next, with the charge transport layer kept at each of the temperatures shown in Table 7, the charge generating layer coating solution obtained in example 1 was applied onto the surface of the charge transport layer (Sample Nos.25 to 30). After that, the coating solution layer was dried by heating at 110° C for 30 minutes to form a charge generating layer of 0.5 µm thickness.

The surface condition of the charge generating layer coating solution applied on the surface of the charge transport layer was examined, the results of which are shown in Table 7.

In Table 7, X indicates that cracks were caused in the charge transport layer, O indicates that the surface condition of the charge transport layer was good, and (X) indicates that irregularities were noted on the charge transport layer.

Table 7

No.	Tg of the charge transport layer (° C)	Charge transport substance	Heat retaining temperature (° C)	cracks
19	74	A	23	×
20	74	A	31	×
21	74	A	33	○
22	74	A	40	○
23	74	A	70	○
24	74	A	77	(×)
25	66	B	23	×
26	66	B	31	×
27	66	B	33	○
28	66	B	40	○
29	66	B	65	○
30	66	B	70	(×)
1,1-diphenyl-4,4-di(diethylamino)phenyl-1,3-butadiene •••A ethyl carbonate-diphenylhydrazone •••B				

From Table 7, it was confirmed that a photoconductor having a good surface condition can be obtained when the charge generating layer coating solution is applied on the charge transport layer with the charge transport layer kept at a temperature higher than 33° C and lower than the glass-transition temperature (Tg) of the charge transport layer.

Claims

1. A method for manufacturing an electrophotographic organic photoconductor, comprising the steps of: forming on the surface of a conductive base a charge transport layer consisting of a first resin composition; and forming on the surface of said charge transport layer a charge generating layer consisting of a second resin composition,
wherein the step of forming said charge transport layer includes: the application of a charge transport layer coating solution containing said first resin composition and a solvent onto the surface of said conductive base for the formation of a layer of said coating solution; and
the heat treatment of said coating solution layer at a temperature higher than the glass-transition temperature (Tg) of said first resin composition and lower than the melt-starting temperature of said first resin composition.

2. A method for manufacturing an electrophotographic organic photoconductor, comprising the steps of: forming on the surface of a conductive base a charge transport layer consisting of a first resin composition; and forming on the surface of said charge transport layer a charge generating layer consisting of a second resin composition,
wherein the step of forming said charge generating layer includes: the application of a charge generating layer coating solution containing said second resin composition and a solvent onto the surface of said charge transport layer for the formation of a layer of said coating solution; and
the heat treatment of said coating solution layer at a temperature lower than the melt-starting temperature of said first resin composition.

3. A method for manufacturing an electrophtographic organic photoconductor, comprising the steps of: forming on the surface of a conductive base a charge transport layer consisting of a first resin composition; forming on the surface of said charge transport layer a charge generating layer consisting of a second resin composition; and forming on the surface of said charge generating layer a surface protective layer

consisting of a third resin composition.

wherein the step of forming said surface protective layer includes: the application of a surface protective layer coating solution containing said third resin composition and a solvent onto the surface of said charge generating layer for the formation of a layer of said coating solution; and

the heat treatment of said coating solution layer at a temperature lower than the melt-starting temperature of the charge transport layer consisting of said first resin composition.

4. A method for manufacturing an electrophotographic organic photoconductor, comprising the step of forming a resin layer on the surface of a conductive base,

wherein the step includes the application of a coating solution containing a solvent and a binding resin made of a thermosetting resin and the drying of a layer of said coating solution under prescribed conditions,

said prescribed drying conditions being determined by examining the reduction of a reactive group present in said thermosetting resin by means of infrared absorption spectroscopy.

5. A method for manufacturing an electrophotographic organic photoconductor according to Claim 4, wherein said thermosetting resin is a silicone resin having a silicone oligomer as the main component.

6. A method for manufacturing an electrophotographic organic photoconductor, comprising the steps of: forming on the surface of a conductive base a charge transport layer consisting of a first resin composition; and forming on the surface of said charge transport layer a charge generating layer consisting of a second resin composition,

wherein the step of forming said charge generating layer includes the application and drying of a charge generating layer coating solution containing said second resin composition and a solvent onto the surface of said charge transport layer while holding the base with said charge transport layer formed thereon at a temperature within the range of 33° C to the glass-transition temperature (Tg) of said first resin composition.

Fig. 1

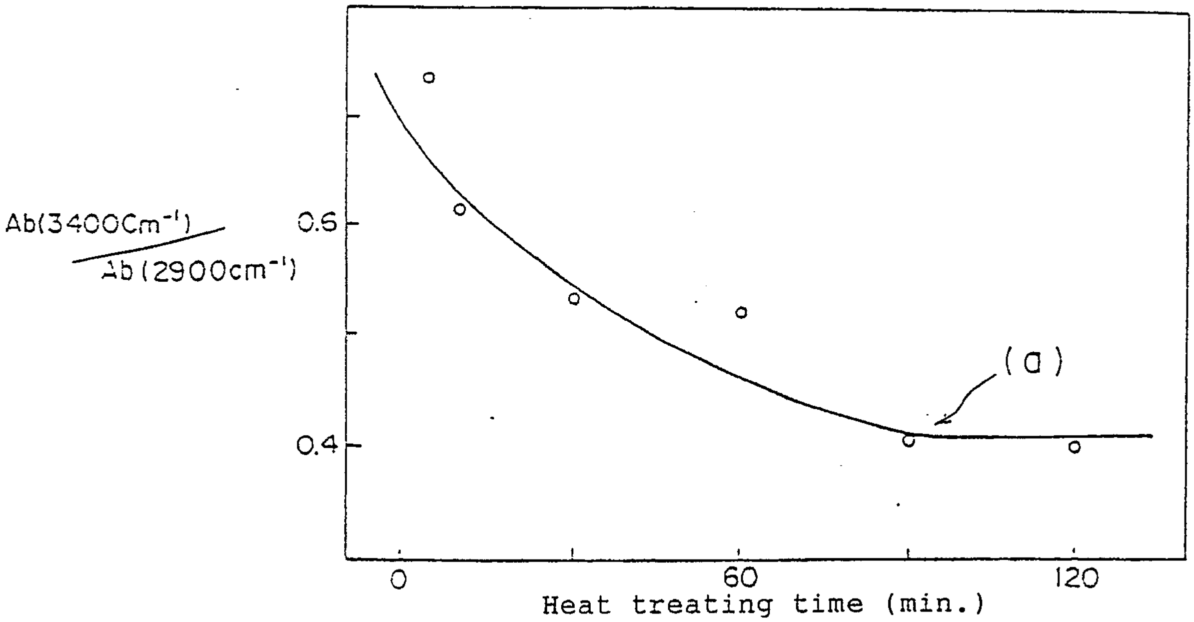

Ab(3400Cm⁻¹)
Ab(2900cm⁻¹)
0.6
0.4
(a)
0
60
120
Heat treating time (min.)

Fig. 2

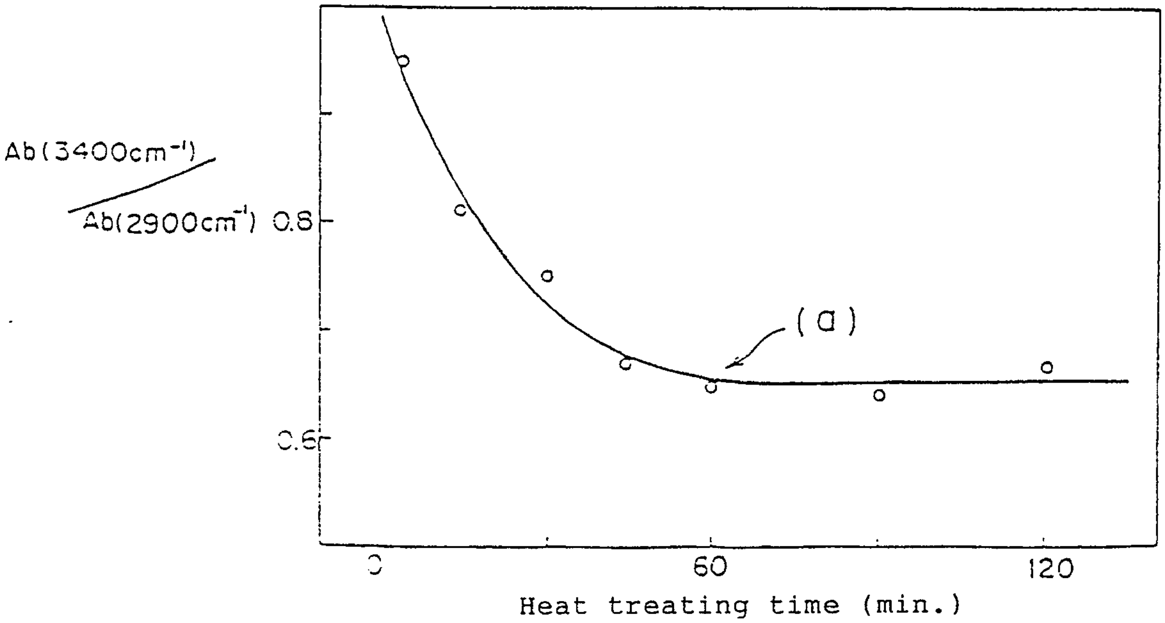

Ab(3400cm⁻¹)
Ab(2900cm⁻¹)
0.8
0.6
(a)
0
60
120
Heat treating time (min.)

Fig. 3

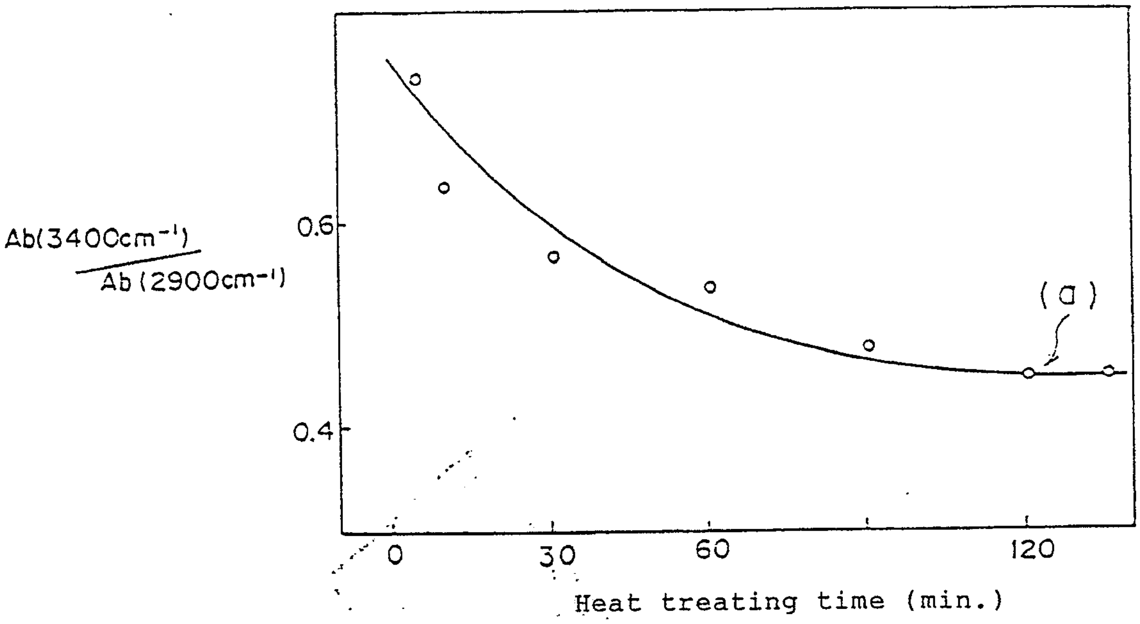

Ab(3400cm⁻¹) / Ab(2900cm⁻¹)
0.6
0.4
(a)
0
30
60
120
Heat treating time (min.)

Fig. 4

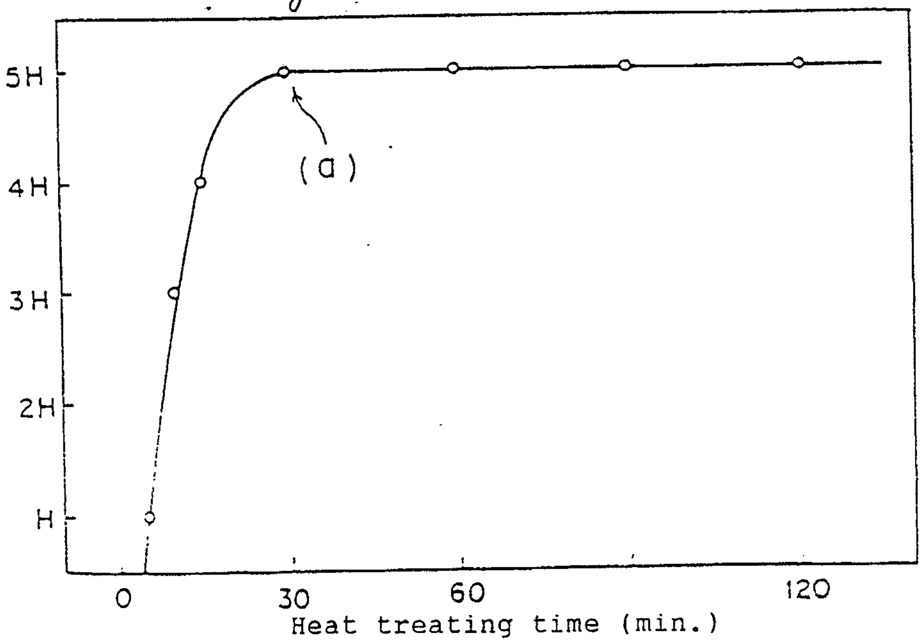

5H
4H
3H
2H
H
(a)
0
30
60
120
Heat treating time (min.)

Fig. 5