

[54] **PROCESS FOR PRODUCING A DRUM
PHOTOSENSITIVE MEMBER FOR
ELECTROPHOTOGRAPHY**

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2,027,962	1/1936	Currie.....	117/94
2,256,777	9/1941	Kaulen.....	117/94
2,626,222	1/1953	Spencer.....	117/94
2,901,348	8/1959	Dessaner et al.	96/1.5
2,962,375	11/1960	Schaffert.....	96/1.2
2,970,069	1/1961	Adams.....	117/94 X
3,046,156	7/1962	Kaulen.....	117/94
3,071,496	1/1963	Fromm et al.	117/218
3,251,686	5/1966	Gundlach.....	117/218 X
3,314,450	4/1967	Doering et al.	117/94
3,457,070	7/1969	Watanabe et al.	96/1 X
3,536,483	8/1965	Watanabe et al.	96/1

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117/94, 117/119.6, 117/218

[51] Int. Cl. **G03b 5/08, B05b 13/06**

[58] Field of Search **96/1, 1.5, 1.2; 117/34,**
117/94, 218, 119.6

[56] **References Cited**

UNITED STATES PATENTS

1,800,360 4/1931 Schroeder..... 117/94

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Kelton & Taggart

[57]

ABSTRACT

A drum photosensitive member for electrophotography is produced by applying a photosensitive material liquid, an electrically insulating translucent material liquid and others to an electrically conductive drum by relatively rotating the drum and the applying means.

8 Claims, 7 Drawing Figures

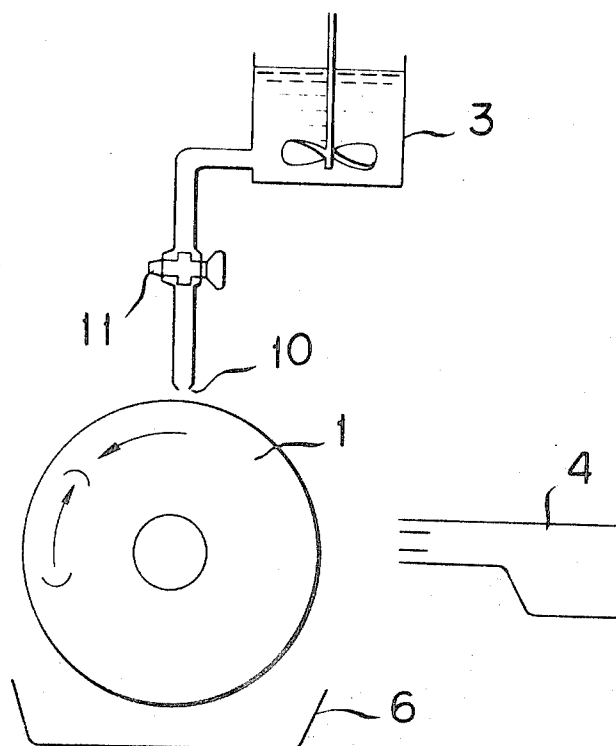


FIG. 1

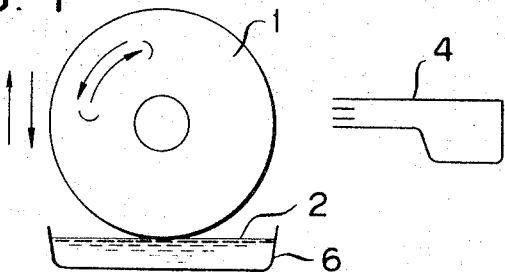


FIG. 2

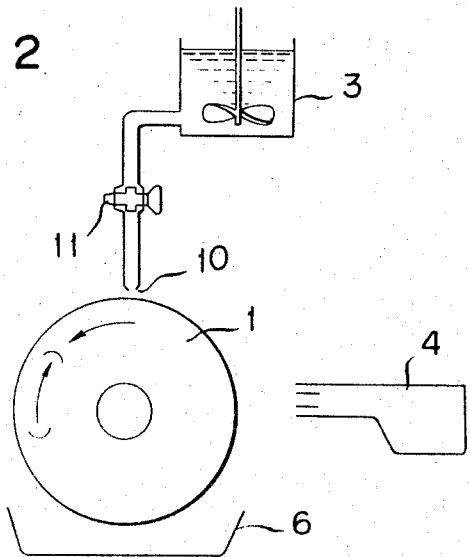
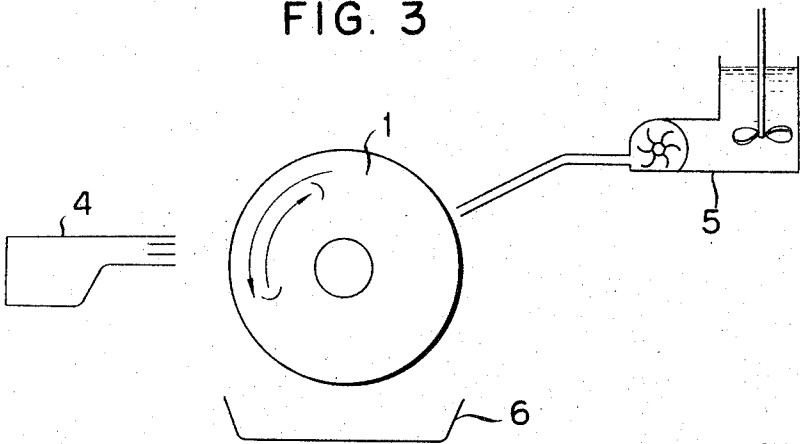


FIG. 3



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FIG. 4

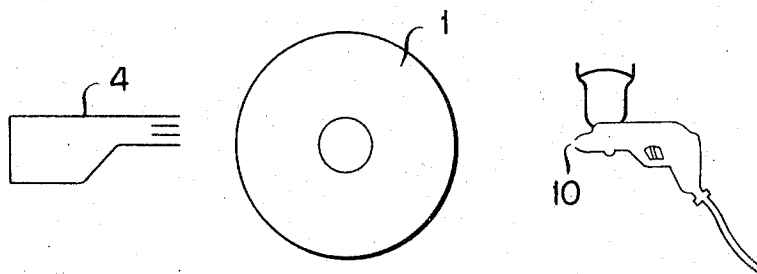


FIG. 5

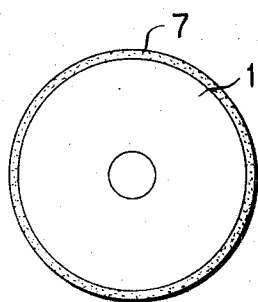


FIG. 6

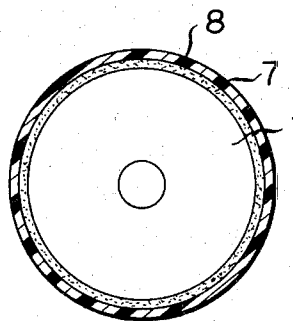
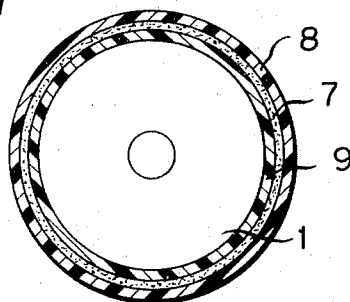


FIG. 7



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PROCESS FOR PRODUCING A DRUM PHOTOSENSITIVE MEMBER FOR ELECTROPHOTOGRAPHY

This invention relates to an electrophotographic drum photosensitive member.

The electrophotographic drum photosensitive member of this invention is used as a photosensitive member by building the same into an electrophotographic copier.

The electrophotographic drum photosensitive member is produced by forming the layer of electrophotographic photosensitive material on the surface of a drum while rotating said drum having the central rotary shaft, then forming an electric insulating translucent layer thereon while rotating the drum, and if necessary, providing an electric insulating layer between a drum and an electrophotographic layer wherein said electrophotographic drum photosensitive member is composed of three or four layers, and has no joint between the electrophotographic photosensitive layer and electric insulating translucent layer.

At least the surface of the drum base can be earthed and is conductive. For example, a metal drum made of iron, copper, aluminum, etc., or the drum made of plastic, glass, wood or such like non-conductive materials whose surface is coated with conductive paints or sputtered with metal, or non-metal drum whose surface has been metal-plated, or non-metal drum provided with metal foil on the surface thereof to give conductivity, can be used.

The central shaft for rotating the base drum may be of such a type as can be removed from the drum base, or may be of such a type that the central shaft is united to the drum base and, after the drum photosensitive member is formed, the central shaft and the drum is built in the copier. The size precision of the drum base is related to the thickness precision of the photosensitive material and the focal depth of the optical system of the copier, and they should be sufficiently precise.

For example, when the diameter of the drum is 150 mm, the tolerable error of the real circularity thereof against the diameter and the parallelism of the drum must be respectively below $\pm 1.5/100$ mm. It is preferable to polish the surface of the drum after the drum has been cut out.

As the electrophotographic photosensitive materials to be applied onto the surface of the drum base, photoconductive materials are used. For example, as inorganic compounds, zinc oxide, titanium dioxide, cadmium sulfide, zinc sulfide, cadmium selenide, zinc selenide, zinc telluride, antimony-cadmium, etc. are used, and as the organic compounds, pyrene, perylene, tetracene, pentacene, ovalene, isoviolanthrene, p-phenylbenzene, 4-phenyl-stilbene, etc., are used.

In applying the respective photoconductive materials onto the drum base, they are used in the form of paints, or varnish, and when the photoconductive materials are in the form of pigment, they are made in the form of paints by using binder resins, and if necessary, resin solvents, and when they are of homogeneous system, they are used in the form of varnish by using a solvent.

Homogeneous photoconductive materials are preferable as the photosensitive materials, but when pigment systems are used, the granularity thereof on the surface

of the photosensitive layer is preferably smaller, and the mean granularity of from 0.1 to 15 μ are preferred.

The mean granularity of the pigment systems to be used in this invention is determined, to a certain extent, depending on the kinds of the photoconductive materials. For example, in the case of zinc oxide, it is from 0.1 to 1 μ and in the case of cadmium sulfide, the larger mean granularity is employed.

The binder resins for obtaining a paint-form photosensitive material are used for producing photosensitive layer by fixing the photoconductive materials after having dry-solidified photosensitive materials, and therefore, it is preferable to apply as less amount of binder as possible when compared with the amount of the photoconductive material so as not to impair the photoconductivity of the photoconductive material.

Generally speaking, from 8 to 40 parts by weight of solid binder on the basis 100 parts by weight of photoconductive material brings about preferable result.

The resin materials used as the binder are those having high electric insulating property when dried, high film forming property, high adherability onto the drum base and photoconductive materials, and are solid and stable at a room temperature, under atmospheric pressure, and for example, phenol resin, urea resin, alkyl resin, silicon resin, acryl resin, polyester resin, methacryl resin, styrol resin, cumarone-indene resin, epoxy resin, formal resin, polyvinyl acetate (or chloride), polyvinyl acetate-vinyl chloride copolymer, cellulose acetate (or nitrate), shellac, zein, casein, polyvinyl alcohol, cellulose ether, cinnamic acid ester, glue etc., may be used.

In order to obtain a paint-form photosensitive material liquid, the combination of the kinds of photoconductive materials, the kinds of binder resins, the kinds of the solvents for binder resins, and the method for dispersing photoconductive materials should be most carefully selected.

The combination is selected in relation to the properties of the respective materials and the method for coating on the rotary drum.

With respect to the materials, for example, when zinc oxide is used as photoconductive material, it is preferable to carry out dispersion of silicon resin varnish (xylol solvent) as the binder resin by using of a roller mill or ball mill, and when cadmium sulfide is used as the photoconductive material, it is preferable to carry out dispersion of a polyvinyl acetate-vinyl chloride copolymer containing a lacquer thinner as the binder resin by using a homogenizer.

When a photoconductive material is homogeneous, a varnish-form photoconductive material is prepared by using a solvent, and it is coated on a rotating drum.

Next, explanation is given about the method for applying a photosensitive material onto the surface of drum base referring to the drawing wherein:

FIGS. 1, 2, 3, and 4 are the diagrams showing the apparatus for producing drum photosensitive member of this invention;

FIG. 5 is a cross sectional view showing the state in which photosensitive material layer is formed on a drum by using said apparatus;

FIG. 6 is a cross sectional view showing the state in which the electric insulating translucent layer is formed on the photosensitive layer; and

FIG. 7 is a cross sectional view showing the state in which electric insulating layer is formed between the photosensitive material layer and the drum and an electric insulating translucent layer is formed on the photosensitive layer.

In FIG. 1, the surface of the photosensitive liquid 2 is contacted with surface of the drum base 1 while rotating the drum 1 having a central shaft, and when the surface of the drum is uniformly coated with the photosensitive liquid, the contact is dried by means of hot air sent from the fan 4, or by placing the coated drum in an air drier, or by naturally drying the coating, or by coemploying said drying methods. The selection depends on the property of the photosensitive liquid to be applied.

In contacting the drum with the surface of photosensitive liquid, the contact can be carried out while rotating the drum, or the rotation can be started after the contact.

When the liquid of photosensitive material is heterogeneous such as dispersion, precipitation is easily brought about in the liquid more often than not, depending on the granularity, specific gravity or the form of the photoconductive material, and in such a case as this, the liquid is preferably stirred slowly.

As other method for coating, coating is carried out by flowing down the liquid of photosensitive material from the nozzle 10 through the cock 11 from the stock tank 3 placed over the rotary drum as is shown in FIG. 2, and the coating is dried by the hot air sent from the fan 4, or by air bath drying process to dry the coating layer.

In this case, when the liquid of photosensitive material is dispersion, the normal flow-down of the liquid can be prevented by the precipitation of photoconductive material at the place where the nozzle 10 is positioned depending on the properties of the liquid even if the stirring operation should be sufficiently carried out in the stock tank 3.

In such a case, the liquid of photosensitive material is jetted onto the rotating drum by means of jetting means 5 inclusive of a pump from the nozzle 10 directed towards the drum and thereby coating can be carried out (cf. FIG. 3).

On the other hand, as another method for jetting photosensitive liquid, there is such a method according to which coating is effected with liquid spray by coemploying air stream along with the liquid of photosensitive material as is shown in FIG. 4.

It is important regardless which method should be taken, that the thickness of the layer of the photosensitive material after having been dried, should be uniform that the coating should be of uniformity, that the surface of the coating should be as smooth as possible, and that there is no pin hole or such like drawbacks on the coating, and these factors are different in accordance with the composition of the liquid, the method of coating or drying conditions. In this sense, when photoconductive materials of homogeneous system should be used as the photosensitive liquid, there is no problem, but in the case of using a dispersion system, it is recommended to use a dispersion containing larger amount of binder resin.

However, as the amount of binder resin is increased, the properties of photoconductive photosensitive layer are deteriorated accordingly, and therefore it is practi-

cal to have the amount of binder resin to be from 8 to 40 percent.

As the method of coating, when the mean granularity is less than $1\ \mu$ or it is of homogeneous system, the surface coating as is shown in FIG. 1, or the liquid spray by coemploying air stream as is shown in FIG. 4 are preferable.

However, when the mean granularity is as large as several microns, the liquid flowing method or liquid spraying method shown in FIG. 2 and FIG. 4 are preferable.

In order to smooth the surface of the coating and to prevent pin holes, the method for drying the coating is also counted as an important factor.

Drying is carried out while slowly rotating the drum, but quick drying should be avoided.

For example, when the photosensitive liquid has been uniformly applied to the surface of rotating drum, the further supply of the photosensitive liquid is stopped, and the rotation of the drum is kept on for a time being at the room temperature, and after the photosensitive liquid is fast set on the surface of the drum, said drum is put into an air bath while rotating the same and is slowly heated or it is preferable to dry sufficiently by slowly raising the temperature while sending hot air.

Of course, depending on the kind of the solvent, it is possible to carry out hot air treatment or air bath treatment directly after applying the coating, and a better result can be obtained sometimes, but quick drying should be avoided as far as possible.

As another means for preventing quick drying of coating, it is also effective to add a solvent of low vapor pressure for preventing quick drying into the solvent contained in the photosensitive liquid.

In general, as the solvents for photosensitive liquid, xylol, toluol, alcohol, methylethyl ketone, trichloroethylene, ester etc., can be used, but these solvents are of high vapor pressure and of low boiling point, and cause pin holes, cracks, or coating irregularity because of the quick drying caused thereby.

On the other hand, when a solvent of low vapour pressure having mutual solubility with said solvents and the material to be dissolved is added thereto, it is possible to suppress the quick drying at the time of coating, and thereby it is possible to attain the uniformity of the coating, the preventing of pin holes, and the smoothness of the surface.

As the examples of the solvents for preventing quick drying, the following solvents can be given:

cyclohexanone,
ethylbutylketone,
isopropylbenzene,
tetrachloroethane,
ethylene chlorohydrin,
n-butyl alcohol,
sec-hexyl alcohol,
isopropyl alcohol,
ethylene glycol monobutyl ether,
diethylene glycol monoethyl ether,
methylanil acetate,
methyl acetoacetate,
isoamyl propionate,
ethyl lactate, etc.

The appropriate solvents for preventing quick drying must be selected by taking the properties of binder resin, the properties of neighbouring coatings in the

case of multilayer coating and the method for coating into consideration.

The thickness of the coating of photosensitive material is generally from several microns to 100 microns, but it is difficult to obtain smooth layer whose thickness is above ten microns by one coating process in most cases.

In such a case, the first layer is applied, and after having dry-solidifying the first layer or after having the first layer set, the second layer is applied.

In carrying out this method, the liquid of photosensitive material of the second layer should be one which cannot be easily mutually dissolved with the first layer coating.

For example, when the binder resin of the first layer is styrol resin and xylol is selected as the solvent therefor, shellac is selected as the binder resin of the second layer and ethyl alcohol is selected as the solvent therefor.

On the other hand, when such a resin as epoxy resin, polyester having such a property as to be hardened by a hardening agent, is used as binder resin, the second layer can be applied after having hardened the first layer, and therefore in such a case, the composition of the first layer and that of the second layer can be made exactly the same.

When the third layer is required, the liquid having no mutual solubility with the coating of the second layer can be applied to form the third layer.

When the third layer is coated, the liquid of the same composition as the first layer can be employed.

In the same manner, the composition of the fourth layer can be the same as the composition of the second layer.

Namely, if the respective layers are not easily mutually dissolved into each other, the coating liquid of the same composition can be used for every other layer.

In other words, it is possible to carry out multilayer coating up to a required thickness by using the compositions having no mutual solubility with the adjacent layers.

When multi-layer coating is carried out, it is possible to improve the properties of photosensitive layer by changing the kind of photoconductive material contained in photosensitive liquid, the granularity thereof and the composition of the photosensitive liquid.

For example, photoconductive material of relatively large granularity is coated by using little amount of binder resin to make the lower layer, and photoconductive material of less granularity is coated by using more amount of binder resin to make the uppermost layer and thereby it is possible to produce a smooth photosensitive layer having excellent photosensitivity because of the composition of the lower layer, and smooth sharp sensitivity because of the composition of the upper layer.

FIG. 5 is a cross sectional view showing the photosensitive layer 7 formed on the surface of the drum 1.

A method for forming an electrically insulating translucent layer 8 (see FIG. 6) on the formed photosensitive layer.

The electrically insulating layer on the photosensitive layer is indispensable in the present electrophotography, and a layer whose thickness is about 3 - 40, microns is formed as the electrically insulating layer.

The layer should be smooth on the surface, having no pin holes or irregularity, excellent film forming prop-

erty and excellent surface strength, and should be translucent, and at the same time, have high electric insulation.

The material for the electrically insulating layer can be selected from resins used for general paints.

For example, phenol resin, urea resin, melamine resin, alkyd resin, styrol resin, polyester resin, epoxy resin, acryl resin, polyvinyl acetate (or chloride), polyvinyl-acetate-vinylchloride copolymer, formal resin, cellulose acetate (or nitrate), polycarbonate resin, cellulose ether, silicon resin, polyurethane resin, zein, shellac, etc., can be used.

In regard to the method for forming the electrically insulating translucent layer 8, the same method as the method for forming photosensitive layer 7 can be employed in such a manner that, while rotating the drum base having been provided with the photosensitive layer, a liquid for translucent layer is used in place of the photosensitive liquid in accordance with the methods as shown in FIGS. 1-4.

In other words, the above given translucent material is dissolved to form a varnish form solution by dissolving the translucent material in an appropriate solvent suitable for the respective translucent material, and the obtained solution is put into a receiver 6 as is shown in FIG. 1, and the solution is contacted against the photosensitive layer 7 of the rotating drum 1, and when the photosensitive layer is uniformly coated with the liquid of translucent material, the drum is removed from the liquid surface and the coating is air-dried.

The layer of photosensitive material and the liquid of translucent layer should be selected so as not to damage the photosensitive layer by the solvent to be employed, in such a manner that the composition of the photosensitive layer and the translucent layer cannot be easily and mutually dissolved.

For example, when zein is used as the binder resin for the photosensitive material 7 and the mixture solvent of water and methyl alcohol at the ratio of 8:2 is used, a xylol solution of styrol resin is used for forming the translucent layer 8.

It is a matter of course that the methods for coating as shown in FIG. 2 through FIG. 4 can also be employed in addition to the above.

What is especially important in preparation of the translucent layer is that, pin holes, air-foams, and the local irregularity in the thickness should be avoided in the layer 8, since these become the causes for insulation break-down or irregular charge when voltage is applied in a copier.

To prevent pin holes, the employment of a solvent of low vapor pressure and the adjustment of the conditions for air-drying can attain considerable effect, as in the case of the preparation of photosensitive layer 7.

The solvents used in the preparation of translucent layer can be selected from the solvents of low vapour pressure which are used in producing the photosensitive layer.

In the preparation of the translucent layer, if the thickness of the translucent layer is insufficient by one coating process, the second layer may be formed on the surface of the translucent first layer by using a liquid having a composition which hardly mutually dissolves the first layer, and when it is still insufficient, the third layer is applied to the second layer by using a liquid of a composition which hardly mutually dissolves the second layer, and in the same manner a translucent multi-

layer can be formed by using the liquid of the composition which cannot be easily mutually dissolved into the neighbouring layers.

FIG. 6 shows the state in which the photosensitive layer 7 is formed on the drum base 1, and the electric insulating translucent layer 8 is formed thereon.

In accordance with the present electrophotography, an image of high contrast may be obtained by a copier by using the drum photosensitive member of FIG. 6.

In order to copy a photographic image of continuous tone, a photosensitive member of uniform electric charge distribution is required. For this purpose, a thin layer 9 of electric insulation is formed as is shown in FIG. 7 between the drum base 1 and the photosensitive layer 7 to obtain excellent result.

The material of said thin layer 9 may be selected from the materials used for translucent layer 8. The thin layer 9 does not require any special translucent, and therefore it can be prepared by mixing fine powder of silica or mica having high dielectric constant, and originally dark colored resins such as asphalt or pitch may also be used.

The formation of said thin layer 9 on the drum base may be carried out in accordance with the rotary drum system, or it may be formed by winding an electric insulating film around the drum base when such photosensitive layer and translucent layer are applied in such a manner that the effect of the joint portion of the translucent layer 8 is eliminated. As the films to be wound to form the thin layer, for example, films of polyethylene, polycarbonate, polyethylene terephthalate, acetate, polypropylene, polyvinyl chloride may be used.

When thin layer 9 is formed by using a resin solution, a rotary drum is used as is employed in forming the photosensitive layer 7 or the translucent layer 8.

It is needless to mention here that such a composition that is mutually dissolved and reacted with the photosensitive material 7 and the surface material of the drum base 1 can not be used as a liquid for making the thin layer 9.

It is preferable, of course, that the properties of the coating of the thin layer should be free from the drawbacks such as irregularity in thickness of coating or pinholes, but, in this case, it is not necessary that the thickness of the thin layer is so precise as that of the photosensitive layer or translucent layer. Therefore, melt-coating of the coating material or quick air-drying can be employed.

When an electric insulating film is wound up thereon, an adhesive suitable for each film for example, nitrile rubber type adhesive for a polyethylene terephthalate film, is used and the film which is cut into a predetermined size is wound on and adhered to the drum base 1. Since a coating solution for the upper layer (photosensitive layer) is apt to leak through the fine gap at the joint part, the adhesive and the photosensitive layer material should be selected so as to avoid such leak.

When a thermally shrinkable film is used as the film to be wound thereon, a tube-form film of such a size as the drum base can be easily inserted thereinto is shrunk by means of hot air or liquid to the effect that the tube form film is closely contacted on the drum base and a seamless electrically insulating thin layer 9 can be obtained.

As the examples of the above given thermally shrinkable films, polyvinyl chloride film, polyethyleneterephthalate film, and polypropylene film are given.

When the thickness of the thin layer 9 is below 20 microns, excellent result can be obtained.

The following are the examples to further illustrate this invention.

Example 1

10 Composition of the photosensitive material:

Zinc oxide for electrophotography	100	parts by weight
Polystyrene (the trade mark thereof being Piccolastic D-125, produced by Esso)	15	do.
Toluene	100	do.
High boiling point solvent (the trade mark thereof being Solvesso 100)	30	do.

The respective components were treated in a ball mill for about 15 hours, and the resulting liquid was placed in the receiver, and was contacted against the rotary drum which diameter is 15 cm. which was rotated at the speed of 20 rpm, and after the surface of the drum was uniformly wetted by the liquid, the drum was removed from the liquid and was dried with a hot air while rotating the same.

After having dried the drum, the liquid of the following composition was placed in the receiver in the same manner, and was applied on the rotating photosensitive layer to form a translucent film.

The composition of the translucent layer:

Ethyl cellulose (the trade mark thereof being Ethocell produced by Hercules Powder Company)

Ethyl alcohol	10	parts by weight
Ethylene glycol monoethyl ether	150	do.
	30	do.

The above prepared translucent layer was dried with about 70°C hot air while rotating the drum, at 100 rpm, to prepare the cylindrical photosensitive matter for electrophotography.

Thereafter, the prepared photosensitive matter was built in the copier, and about 8 KV positive corona discharge was carried out, and then about 7 KV negative corona discharge and image wise exposure were carried out simultaneously by a slit system, and the toner development was carried out in accordance with magneto brush development. Then, a copying paper was pressed onto the developed image to transfer the toner image onto the surface of the paper, and it was thermally fixed and the image quality of the obtained copy was excellent.

Example 2

The composition of the photosensitive material:

Photoconductive cadmium sulfide	50	parts by weight
Vinyl acetate-vinyl chloride copolymer	5	do.
Ethyl acetate	20	do.
Methylamyl acetate	5	do.

The respective components were uniformly dispersed by using a stirrer.

The photosensitive liquid was poured onto the drum while rotating the drum at 20 rpm, and then it was dried with hot air.

The liquid for translucent layer of the following composition was poured onto the above prepared layer, and then it was dried.

The composition of the translucent layer

Zein	10	parts by weight
Isopropyl alcohol	80	do.
Water	20	do.

After having dried the same, copying was carried out in the same manner in Example 1, and excellent image was obtained.

Example 3

Composition of photosensitive material:

Photoconductive cadmium sulfide	50	parts by weight
Polyvinyl alcohol	5	do.
Water	30	do.

The respective components were uniformly mixed by using a stirrer.

The rotation of the drum was adjusted to be about 50 rpm. and the photosensitive liquid was poured onto the drum and it was dried with 70°C hot air.

Therefore, the liquid for translucent layer of the following composition was poured onto the rotating drum and it was dried with air, and a translucent layer was produced.

The composition of translucent layer

Rosin modified phenol resin (the trade mark thereof being Hitanol produced by Hitachi Chemical Ind. Co.)	10	parts by weight
Xylol	50	do.
High boiling point solvent (Solvesso-100 produced by Esso)	10	do.

After having dried the translucent layer, a copying operation was carried out in the same manner as in Example 1, and excellent image was obtained.

Example 4

Composition of the photosensitive material:

Photoconductive cadmium sulfide	50	parts by weight
Epoxy resin (the trade mark thereof being Epikote No. 828 produced by Shell)	5	do.
Diethylene triamine	0.4	do.
Methylethyl ketone	20	do.

In this case, the hardening time of epoxy resin is long, and it performed the role of preventing pin-holes, and therefore, an evaporation delaying solvent was not added thereto.

After having removed the solvent with a hot air on the rotating drum, epoxy resin was hardened at 70°C in a drying chamber for about 5 hours.

Thereafter, the solution of the following composition was poured onto the rotating drum to be air-dried, and the translucent layer was obtained.

The composition of the translucent layer:

Polystyrene (the trade mark thereof being Piccolastic-D125 produced	
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-Continued

by Esso)	15	parts by weight
Toluene	100	do.
High boiling point solvent (the trade mark thereof being Solvesso-100)	30	do.

The copying operation was carried out in the same manner as in Example 1, and excellent image was obtained.

Example 5

A liquid for preparing translucent layer which was used in Example 2 was applied to the surface of the aluminum rotary drum of Example 2 while rotating said drum, and the coating was dried in an air-bath at 70°C to form an electric insulating layer whose thickness was about 8 microns, and then the photosensitive layer and electric insulating translucent layer were produced on the electric insulating layer obtained above in accordance with the procedure of Example 2.

Copying operation was carried out in the same manner as in Example 1 to produce a drum photosensitive member of uniform chargeability which is suitable for forming photographic images.

Example 6

Thermally shrinkable vinyl chloride tube (Hishilex produced by Mitsubishi Resin Mfg. Co., Ltd.) whose diameter is 180 mm was placed on aluminum drum base whose diameter is 150 mm, and said vinyl chloride tube was shrunk with a 95°C hot water to closely contact with said drum base and the thin electric insulating layer was provided on the conductive drum base, and photosensitive material and electric insulating translucent layer of the same compositions as in Example 2 were applied to the drum while rotating the rotary drum.

After the coated layer was perfectly dried up, the copying operation was carried out in the same manner as in Example 1 and a photosensitive drum of uniform chargeability suitable for the formation of photographic image was obtained.

Example 7

Doughtight, i.e., conductive carbon paint (produced by Fujikura Chemical Ind. Co., Ltd.) was applied to a drum (the diameter thereof being 150 mm, the length thereof being 250 mm) made of Formal resin having an iron central shaft, while rotating said drum in such a manner that the end surface of the drum could be electrically connected with the central shaft, and thereafter it was dried, and the photosensitive liquid composed of the following composition was applied to the surface of the above obtained layer, while rotating the drum.

Composition

Cadmium sulfide activated with copper	100 parts
Zein	15 parts
Isopropyl alcohol	80 parts
Water	20 parts

Thereafter, the coating was air-dried, and then on thus obtained photosensitive layer, the solution of the following composition was applied as electric insulating translucent layer while rotating the drum.

Composition

Rosin modified phenol resin, Hitanol 30G (Produced by Hitachi Chemical Ind. Co.)	10 parts
Xylol	50 parts
Solvesso (Produced by Esso)	10 parts

Thereafter, the coating was air-dried.

Thus obtained drum photosensitive member was used in the electrophotographic copier as in Example 1, and excellent image was obtained.

Example 8

Soft aluminum whose thickness (No. 15 microns was wound up on the surface of a drum (the diameter thereof being 150 mm, the length thereof being 250 mm) having an iron central shaft, prepared by Epoxy resin casting No. 828 made by Shell Chemical Ind. Co., Ltd.) by using Epoxy resin (No. 815 made by Shell Chemical Ind. Co., Ltd.) as the adhesive.

Photosensitive layer and electric insulating translucent layer were formed on the above prepared aluminum layer in the same manner as in Example 1, and image copying was carried out by using an electrophotographic copier and excellent result was obtained.

Example 9

The liquid of photosensitive material composed of the following composition was applied to the surface of an aluminum drum (the diameter thereof being 150 mm, the length thereof being 250 mm) having a central shaft while rotating the drum, and the resulting coating was dried.

Composition

Cadmium sulfide activated with copper (mean granularity thereof being 15 microns)	100 parts by weight
Vinyl chloride-vinyl acetate copolymer (solid portion)	15 parts by weight
Butyl acetate	70 parts by weight

Thus, the first layer having coarse surface was prepared.

Thereafter, the liquid of the photosensitive materials for the second layer composed of the following;

Composition:

Cadmium sulfide activated with copper (mean granularity being 8 microns)	100 parts	by weight
Zein	20 parts	do.
Isopropyl alcohol	80 parts	do.
Water	10 parts	do.

was applied to drum while rotating said drum, and the coating was dried up, and after having perfectly dried up the coating, the liquid of the photosensitive materials given below was applied to the above obtained photosensitive layer while rotating said drum.

Composition

Cadmium sulfide activated by copper (mean granularity thereof being 2 μ)	100 parts by weight
Vinyl chloride-vinylacetate copolymer (solid portion)	25 parts by weight
Butyl acetate	70 parts by weight
cyclohexanone	20 parts by weight

Thereafter, the photosensitive layer was dried to form the third layer.

The surface of the third layer was smooth and uniform.

5 The thickness of the whole photosensitive layer composed of the first photosensitive layer to the third photosensitive layer was about 80 microns.

The solution composed of the following composition was applied to the surface of the above obtained photosensitive layer as an electric insulating translucent layer while rotating the drum.

Composition

15 Zein	10 parts
Isopropyl alcohol	80 parts
Water	20 parts

Then the coating was perfectly dried up to form the uppermost layer.

20 Composition

Rosin modified phenol resin (Hitanol 30 G, produced by Hitachi Chemical Ind. Co.)	10 parts
Xylol	70 parts
25 Solvesso-100 (produced by Esso)	15 parts

The thickness of the whole electric insulating translucent layer was about 40 microns.

30 Thus obtained drum photosensitive member has excellent chargeability to give high contrast image and excellent result is obtained through the same copying operation as in Example 1.

Example 10

35 The photosensitive liquid having the following composition was applied to the surface of an aluminum drum having a shaft (diameter thereof being 150 mm, the length thereof being 250 mm) while rotating said drum.

40 Composition

Cadmium sulfide activated with copper	100 parts by weight
Epoxy resin No. 815 (produced by Shell Chemical Ind. Co., Ltd.)	15 parts
Epoxy hardening agent H-92 (produced by Nihon Gosei Kako)	3 parts
Methylethyl ketone	50 parts
Methylisobutyl ketone	10 parts

50 After having the solvent dried up, the drum was heated in a 70°C air bath for one hour, and Epoxy resin which was a binder resin, was hardened.

After having returned the drum to the room temperature, the second layer was applied by using the photosensitive liquid while rotating the drum. The coating was dried up, heated, and hardened in the same manner as in the first layer, and then the solution of the following composition was applied thereto as an electric insulating translucent layer while rotating said drum, and solvent was evaporated at the room temperature.

60 Composition

Epoxy resin No. 815 (produced by Shell Chemical Co., Ltd.)	100 parts by weight
65 Epoxy hardening agent H-92 (produced by Nihon Gosei Kako)	20 parts
Methylethyl ketone	300 parts
Methylisobutyl ketone	50 parts
Diisobutyl ketone	5 parts

Thereafter, it was heated in a 70°C air bath for 1 hour to harden Epoxy resin.

A solution of the same composition was applied to the resulting layer while rotating the drum. Thereafter, the solvent was evaporated at the room temperature in the same manner as in the first layer, and then the coating was heated in 70°C air both for one hour to harden Epoxy resin to prepare an electric insulating translucent layer.

Thus obtained drum photosensitive member was used in copying operation in the same manner as in Example 1, and it proved to be of excellent chargeability to give high contrast and an excellent result could be obtained.

Example 11

In place of the electric insulating thermally shrinkable vinyl chloride provided on the drum made of aluminum in Example 6, the thermally melted pitch having stationary surface was contacted to the surface of a drum while rotating the drum to uniformly apply said pitch, and then the pitch was solidified at room temperature while rotating the drum. Thus the electric insulating layer was obtained.

The photosensitive liquid having the following composition was applied to the above obtained pitch layer while rotating the drum.

Composition:

Cadmium sulfide activated with copper	100 parts
Zein	15 parts
Isopropyl alcohol	80 parts
Water	20 parts

Thereafter, it was dried, and then the solution of the following composition was applied to while rotating the drum.

Composition:

Xylol	50 parts
Solvesso-100 (produced by Esso)	10 parts
Rosin modified phenol resin Hitanol (produced by Hitachi Chemical Ind. Co.)	10 parts

Thereafter it was air-dried, and an electric insulating translucent layer was obtained.

Thus obtained drum was used in image copying operation by using the electrophotographic copier which was used in Example 1, it proved to be the photosensitive drum member of uniform chargeability suitable for copying of photographic image.

Example 12:

In place of the pitch layer on the surface of aluminum drum in Example 11, Polyethylene terephthalate film whose thickness is 12 microns Diafoil[(produced by Mitsubishi Resin Mfg. Co., Ltd.)] was wound up on the surface of the drum by using a nitrile rubber adhesive, and the same photosensitive material and the same electric insulating translucent material as in Example 11 were formed in the same manner as in Example 11 to prepared the same photosensitive layer and electric insulating translucent layer, and a drum photosensitive member was produced.

Copying operation was carried out by using the above prepared drum photosensitive member, and it proved to be excellent photosensitive drum member of

uniform chargeability suitable for uniform photographic image.

Example 13:

An aluminum drum (the diameter thereof being 150 mm, the length thereof being 250 mm) having shaft was contacted against the liquid surface of photosensitive liquid having the following composition contained in a vessel to have the drum uniformly coated with the liquid.

Composition:

Zinc oxide	100 parts
Polystyrol Piccolastic D-125 (produced by Esso)	15 parts
Toluol	100 parts
Solvesso-100 (produced by Esso)	30 parts

Thereafter, the drum was separated from the liquid surface, and it was air-dried in 70°C air, and after having dried the same, the drum was contacted against the solution having the following composition while rotating the drum.

Composition:

Ethylcellulose [(Ethocel (produced by Hercules))]	10 parts
Ethylalcohol	150 parts
Ethyleneglycol monomethylether	30 parts

After having uniformly coated the above solution, the contact of the drum against the liquid surface was stopped, and the coating was dried in air with 70°C air stream to produce a drum photosensitive member.

Thus obtained member was used in an electrophotographic copier to carry out copying operation and image copy of high resolution was obtained.

Example 14

After having formed the photosensitive layer in Example 13, the solution having the following composition was sprayed together with air stream at the air pressure of 7 kg/cm² towards the drum from the nozzle at the distance of 60 cm by using a spraying device for coating. Thus coating was prepared.

Composition:

Ethylcellulose Ethocel (produced by Hercules)	10 parts
Ethyl alcohol	200 parts
Ethylene glycol monomethylether	40 parts

Thus obtained coating was air dried, and a drum photosensitive member having an electric insulating translucent layer was obtained.

Copying operation was carried out by using thus obtained drum member, and excellent copies of high image quality could be obtained.

Example 15

An aluminum drum (the diameter thereof 150 mm, the length thereof being 250 mm) with a central shaft was coated with a photosensitive solution having the following composition contained in a vessel having a stirrer by using a gear pump to forcibly jet the solution through a nozzle directed towards the rotating drum.

Composition:

Cadmium sulfide activated with copper	50 parts
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-Continued

Vinyl acetate-vinyl chloride copolymer	5 parts
Butyl acetate	20 parts
Methylamyl acetate	5 parts

After the surface of the drum was uniformly coated with the above solution, the jetting was stopped, and while rotating the drum, it was dried in a 70°C air stream, and the surface of the photosensitive coating was contacted against the surface of the liquid having the following composition in a vessel, while rotating ten drum.

Composition:

Ethylcellulose Ethocel (produced by Hercules)	10 parts
Ethylalcohol	150 parts
Ethylene glycol monoethylether	30 parts

Thus, the solution was uniformly coated on the drum and then it was dried at a room temperature for 2 hours, and it was further air-dried in a 70°C air.

Thus obtained drum photosensitive member was used in copying operation and copies of high contrast were obtained.

Example 16

The photosensitive liquid of the same composition as in Example 1 contained in a vessel with a stirrer was flowed down through a flow amount adjuster to apply the liquid uniformly to the aluminum drum (150 mm in diameter and 250 mm in length) having a central shaft while rotating the drum, and then the flow of the liquid was stopped, and the coating was air-dried, and then while rotating the drum, the flow of an electric insulating solution of Example 1 was applied to the surface of the photosensitive material on the drum by using the liquid spraying device of air stream coemploying type as in Example 14, and after having the electric insulating translucent solution was applied uniformly to the surface of the photosensitive layer on the drum, and the coating was dried.

Thereafter the drum was left out at a room temperature for about two hours, and then it was dried in a 70°C air stream, and the drum photosensitive member was obtained.

When it was used in electrophotographic copier to produce copies, excellent result was obtained.

What is claimed is:

1. A method for providing a drum member for electrophotography comprising the steps of:

- a. providing a drum having an electrically conductive surface;
- b. while rotating said drum, applying to the surface thereof a film of liquid comprising a mixture of particulate photoconductive material, a binder resin, a first solvent therefor, and a second solvent, said second solvent having a lower vapor pressure than said first solvent, said second solvent being employed in quantity sufficient to lengthen the evaporation time of the total solvent, said total solvent comprising said first and second solvents;
- c. evaporating said first and second solvents from said photoconductive liquid film by applying heated air thereto to provide a solid photoconductive layer of less than 100 microns on said drum surface;
- d. while rotating said drum, applying to the surface of said photoconductive layer a film of liquid con-

taining electrically insulative translucent material and a solvent therefor; and

e. evaporating the solvent from said insulative liquid film by applying heated air thereto to provide a substantially imperforate solid translucent insulative layer on said photoconductive layer.

2. The method claimed in claim 1 wherein said first solvent is selected from the group consisting of xylol, toluol, alcohol, methylethyl ketone, trichloroethylene and ester.

3. The method claimed in claim 1 wherein said second solvent is selected from the group consisting of cyclohexanone, ethylbutylketone, isopropylbenzene, tetrachloroethane, ethylene chlorohydrin, n-butyl alcohol, sec-hexyl alcohol, isopropyl alcohol, ethylene glycol monobutyl ether, diethylene glycol monoethyl ether, methylamyl acetate, methyl acetoacetate, isomyl propionate and ethyl lactate.

4. A method for providing a drum member for electrophotography comprising the steps of:

- a. providing a drum having an electrically conductive surface;
- b. while rotating said drum, applying to the surface thereof a film of liquid comprising a mixture of particulate photoconductive material, a binder resin, a first solvent therefor, and a second solvent, said second solvent having a lower vapor pressure than said first solvent, said second solvent comprising from about 15 to about 30 percent by weight of the weight of said first solvent;
- c. evaporating said first and second solvents from said photoconductive liquid film by applying heated air thereto to provide a solid photoconductive layer of less than 100 microns on said drum surface;
- d. while rotating said drum, applying to the surface of said photoconductive layer a film of liquid containing electrically insulative translucent material and a solvent therefor; and
- e. evaporating the solvent from said insulative liquid film by applying heated air thereto to provide a substantially imperforate solid translucent insulative layer on said photoconductive layer.

5. A method for providing a drum member for electrophotography comprising the steps of:

- a. providing a drum having an electrically conductive surface;
- b. while rotating said drum, applying to the surface thereof at least one film of a first liquid comprising a mixture of particulate photoconductive material, a binder resin and a solvent therefor;
- c. evaporating the solvent from said photoconductive liquid film by applying heated air thereto to provide a substantially imperforate solid photoconductive layer of less than 100 microns on said drum surface; d. while rotating said drum, applying to the surface of such first photoconductive layer at least one film of a second liquid comprising a mixture of particulate photoconductive material, a binder resin and a solvent therefor, said particulate photoconductive material of said first photoconductive liquid being of larger granularity than said particulate photoconductive material of said second photoconductive liquid;
- e. evaporating the solvent from said second photoconductive liquid film by applying heated air thereto to provide a second substantially imperfor-

- ate solid photoconductive layer of less than 100 microns;
- f. while rotating said drum, applying to the surface of said second photoconductive layer a liquid containing electrically insulative translucent material and a solvent therefor; and
 - g. evaporating the solvent from said insulative liquid film by applying heated air thereto to provide a substantially imperforate solid translucent insulative layer on said second photoconductive layer.
6. A method for providing a drum member for electrophotography comprising the steps of:
- a. providing a drum having an electrically conductive surface;
 - b. while rotating said drum, applying to the surface thereof at least one film of a first liquid comprising a mixture of particulate photoconductive material, a binder resin and a solvent therefor;
 - c. evaporating the solvent from said photoconductive liquid film by applying heated air thereto to provide a substantially imperforate solid photoconductive layer of less than 100 microns on said drum surface;
 - d. while rotating said drum, applying to the surface of such first photoconductive layer at least one film of a second liquid comprising a mixture of particulate photoconductive material, a binder resin and a solvent therefor, said first photoconductive liquid containing a greater percentage of said binder than said second photoconductive liquid;
 - e. evaporating the solvent from said second photoconductive liquid film by applying heated air thereto to provide a second substantially imperforate solid photoconductive layer of less than 100 microns;
 - f. while rotating said drum, applying to the surface of said second photoconductive layer a liquid containing electrically insulative translucent material and a solvent therefor; and
 - g. evaporating the solvent from said insulative liquid film by applying heated air thereto to provide a substantially imperforate solid translucent insulative layer on said second photoconductive layer.
7. A method for providing a drum member for electrophotography comprising the steps of:
- a. providing a drum having an electrically conductive surface;
 - b. while rotating said drum, applying to the surface thereof at least one film of a first liquid comprising a mixture of particulate photoconductive material, a curing agent, a binder resin and a solvent therefor;
 - c. evaporating the solvent from said photoconductive liquid film by applying heated air thereto to provide a substantially imperforate solid photoconductive layer of less than 100 microns;

- tive layer of less than 100 microns on said drum surface;
- d. while rotating said drum, applying to the surface of such first photoconductive layer at least one film of a second liquid comprising a mixture of particulate photoconductive material, a curing agent, a binder resin and a solvent therefor;
 - e. evaporating the solvent from said second photoconductive liquid film by applying heated air thereto to provide a second substantially imperforate solid photoconductive layer of less than 100 microns;
 - f. while rotating said drum, applying to the surface of said second photoconductive layer a liquid containing electrically insulative translucent material and a solvent therefor; and
 - g. evaporating the solvent from said insulative liquid film by applying heated air thereto to provide a substantially imperforate solid translucent insulative layer on said second photoconductive layer.
8. A method for providing a drum member for electrophotography comprising the steps of:
- a. providing a drum having an electrically conductive surface;
 - b. while rotating said drum, applying to the surface thereof at least one film of a first liquid comprising a mixture of particulate photoconductive material, a binder resin and a solvent therefor;
 - c. evaporating the solvent from said photoconductive liquid film by applying heated air thereto to provide a substantially imperforate solid photoconductive layer of less than 100 microns on said drum surface;
 - d. while rotating said drum, applying to the surface of such first photoconductive layer at least one film of a second liquid comprising a mixture of particulate photoconductive material, a binder resin and a solvent therefor, said solvents of said first and second photoconductive liquids being mutually non-soluble;
 - e. evaporating the solvent from said second photoconductive liquid film by applying heated air thereto to provide a second substantially imperforate solid photoconductive layer of less than 100 microns;
 - f. while rotating said drum, applying to the surface of said second photoconductive layer a liquid containing electrically insulative translucent material and a solvent therefor; and
 - g. evaporating the solvent from said insulative liquid film by applying heated air thereto to provide a substantially imperforate solid translucent insulative layer on said second photoconductive layer.
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