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LIGHT SENSITIVE LAYER FOR ELECTROPHOTOGRAPHY

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6 Claims

ABSTRACT OF THE DISCLOSURE

A light sensitive photographic layer containing photoconductive zinc oxide powder, an electrically insulating film-forming material and a water insoluble cupric compound. A process for forming the light sensitive layer comprises mixing photoconductive zinc oxide powder and a finely divided cupric compound with a solution of an organic film-forming material, and then coating the resulting mixture onto a suitable support.

This invention relates to a novel light sensitive layer for electrophotography using zinc oxide as the photoconductive material.

The characteristics of a light sensitive layer for electrophotography consisting of photoconductive zinc oxide and an electrically insulating film forming material are remarkably influenced by the change of the film forming material which will be designated as a binding agent hereinafter.

Important points required for the electrophotographic characteristics of such a layer are as follows:

- (I) High initial surface potential (a potential just after changing by a corona discharge in a dark place,
- (II) Suitably slow dark attenuation,
- (III) Rapid light attenuation and low residual potential, and
- (IV) No formation of fog during developing.

We have tested a number of binder compositions and found that many of them can be put to practical use. Furthermore, it is found that the degree of influence on the characteristic (I) by radiating light prior to charging is remarkably changed by the nature of the binding agent composition in particular. Therefore, the following condition (V) must be added:

- (V) The effect of pre-exposure to light is hardly suffered or can be eliminated as fast as possible.

A state where the influence by the pre-exposure to light remains is called "light-adapted," while a state where such an influence is eliminated by storing in a dark place for a long time is called "dark-adapted."

When a layer in the light-adapted state (fatigued state) is subjected to corona discharge, the potential is low and the dark attenuation velocity is high. In order to bring this to the dark-adapted state, it is effective to allow it to stand in a dark place for a long time, to heat in a dark place or to subject to a negative corona discharge.

As the corona discharge itself causes a layer to recover from the light-adapted state to the dark-adapted state, it is better, for the correct judgment of the degree of fatigue, to observe a curve of charging time-surface potential rather than to measure an initial surface potential. In a dark-adapted layer, left standing in a dark place for a long time, the rising gradient of the charge curve is high-pitched and the saturation potential value

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is high, while in a light-adapted layer, the gradient is gentle and the saturation potential value is low.

The recovering velocity of fatigue varies to a great extent with a binding agent combined with zinc oxide. We have found as a result of studies that silicone resin is the most excellent in this point but many other resins such as alkyd, epoxy, epoxy ester, copolymer of vinyl chloride and acetate, acrylic acid ester, methacrylic acid ester, polyvinyl butyral, copolymer of styrene and butadiene, sulfonamide and polyketone, and their miscible combinations compare unfavorably with silicone resin, that is, the recovering velocity is much lower. With respect to thermosetting or setting resins, the recovering velocity is lowered after hardening rather than therebefore. We have invented and filed an application about a new method utilizing this phenomenon (Japanese patent application No. 39,489/63). In this invention, effective additives capable of raising the recovery velocity remarkably for any binding agent composition are discovered.

We have now found in accordance with this invention that the fatigue recovering character of electrophotographic elements can be greatly improved by the combination with zinc oxide of a finely divided water-insoluble compound containing cupric ion. This method is more convenient and effective as compared with methods of treating zinc oxide with aqueous solution of inorganic salt.

Illustrative of the effective cupric compound are cupric oxide, cupric sulfide, cupric selenide, cupric hydroxide, cupric carbonate, basic cupric carbonate, cupric phosphate, cupric arsenite, cupric formate, cupric oxalate, cupric oleate, cupric stearate and cupric salts of organic acids.

In a light sensitive layer of zinc oxide in the light-adapted state, the adsorption of oxygen to the surface of zinc oxide is hindered by some factor. That a binding agent retards the recovery is likely due to the mechanism wherein a functional group in the binding agent is adsorbed on the surface of zinc oxide in place of oxygen or ties up available oxygen.

The cupric compound promotes the absorption progress by some mechanism, it is thought. Although it is not clear whether a part of cupric ions is partially doped in the surface of zinc oxide or not, the doping may occur partially considering that a remarkable effect is brought by mixing zinc oxide and a binding agent with cupric ion in an amount of only 0.002% by weight of the zinc oxide.

The amount of cupric salt to give a clear effect may be more than 0.002% of cupric ion by weight of the zinc oxide. The resistance to exposure to light having a high intensity of illumination is produced with the increase of the amount added to zinc oxide. Even if a large amount of such water-insoluble copper compound is added, other electrophotographic characteristics are scarcely influenced. Approximately up to 20% by weight of cupric ion may be added to zinc oxide.

As it has already been known that the fatigue phenomenon is dependent upon the surface layer of a light sensitive layer, the light sensitive layer of our invention may be adapted only to the surface layer, the lower layer being free of the copper compound. In the case of a light sensitive layer having a thickness of about 20 microns, if only the surface layer of 2-5 microns or more is composed of a layer having a high fatigue restoration, the character of this light sensitive layer is represented by that of the surface layer.

Where the binding agent is a setting composition, the fatigue restoration is retarded by the setting in the con-

ventional manner, but the presence of cupric salt improves such defect somewhat.

Among the cupric compounds, cupric stearate has such specific advantage besides the above-mentioned ones that when the stearate is added in the coating liquid for the electrophotographic sensitive layer containing zinc oxide particles, it acts remarkably to prevent the precipitation of the zinc oxide particles as well as easily redisperse precipitated zinc oxide particles in the coating liquid, which improves the stability and the preservability of the coating liquid. That is, a large amount of cupric stearate makes the fluidity of the liquid thixotropic, resulting in the difficulty in some coating methods but preventing, if properly used, the sedimentation of inorganic pigments such as zinc oxide, whereby the storage property of the coating liquid can be improved. Therefore, the use of the stearate together with another copper salt is preferable to bring two or more improvements simultaneously. Of course, combinations of two or more other cupric salts also possible.

Moreover, as the copper compound has such an effect as to improve the dark attenuation character, it will be possible to add a material worsening the dark attenuation character, for example, a sensitizer, the addition thereof being undesired because of this.

This is shown in Examples IV and V, wherein the presence of the copper compound overcomes the disadvantage arising from the use of aluminum stearate alone, which acts to increase the dispersiveness of a pigment but to worsen the dark attenuation character. Similar effect can be found in the joint use with a sensitizing dye.

In addition, the electrophotoconductive layer of the present invention can be used not only for general printings in office but also for marking.

The invention will be more fully understood in the light of the following examples:

EXAMPLE I

Composition A

	Part by weight
Photoconductive zinc oxide powder	100
Soya-bean oil type alkyd resin varnish (soya-bean oil modifying, oil length 40%) (non-volatile 50%)	30
Low polymerization degree silicone resin varnish (non-volatile 60%)	30
Cobalt naphthenate	1.0
Methyl ethyl ketone peroxide	0.5
Toluene	20

The foregoing composition was charged to a ball mill of porcelain and mixed adequately.

Composition B

Composition A was mixed with 0.02 part of cupric sulfide to prepare composition B. The compositions each was suitably diluted with toluene and applied to a wash-primer coated, soft steel plate by spraying to give a coating layer of 20 micron.

After standing for two days at room temperature, they were left standing in a dark place for more than 10 hours, subjected to corona discharge in a dark place, and the electrophotographic characteristics were measured to give the following results. In addition, the pre-exposure to light being given, the restoration characters were studied.

	A	B
Initial surface potential (volt)	450-500	450-500
Half time for dark attenuation (min.)	6-8	8-9
Relative sensitivity for xenon light source	100	70
Initial potential when charged after pre-exposure to light of 5,000 lux from a fluorescent lamp for 5 min. and standing in a dark place for 2 min. (volt)	70-80	250-300

In B, the sensitivity is somewhat lowered but this does not harm to the practical use. The restoration from the fatigue is faster than in A.

EXAMPLE II

In a similar manner, each of compositions C and D shown below was mixed uniformly, applied to an original paper on which polyvinylpyrrolidone had been subbed, to give a thickness of 15-18 microns (on dry base) and dried.

Composition C

	Part by weight
Photoconductive ZnO powder	100
Silicone resin varnish (non-volatile 60%)	18
Styrene-modified alkyl resin varnish (non-volatile 50%)	32
Toluene	10
Methyl ethyl ketone	10

Composition D

Composition C was mixed with the following components:

	Part by weight
Cupric stearate	0.2
Cupric oxalate	0.2

The characteristics are as follows:

	C	D
Initial surface potential (volt)	450-500	450-500
Half time for dark attenuation (min.)	About 5	About 7
Relative sensitivity for xenon light source	100	90
Initial potential after pre-exposure to light of 500 lux from a fluorescent lamp for 5 min. and standing in a dark place for 5 min. (volt)	100-150	400-460

EXAMPLE III

In a similar manner, the following two compositions were applied to an aluminum plate to give a thickness of 20 microns (dry base):

Lead chromate, 15 part by weight.

Composition E

	Part by weight
Photoconductive zinc oxide	100
Polyvinyl butyral	45
Toluene	60
Ethyl acetate	120
i-Propyl alcohol	20

Composition F

Composition E was mixed with 0.015 part by weight of cupric oxide.

The characteristics were as follows:

	E	F
Initial surface potential (volt)	220-250	250-280
Half time for dark attenuation (min.)	About 3	About 4
Relative sensitivity for xenon light source	100	105
Initial potential after pre-exposure to light of 500 lux from a fluorescent lamp for 5 min. and standing in a dark place for 5 min. (volt)	120-150	200-220

In this case, cuprix oxide was reacted as a sensitizer to some extent.

EXAMPLE IV

As to both compositions of Example II to which 8 ml. of 0.5% solution of Rose Bengal had been added, a similar effect of promoting the fatigue restoration by the addition of copper salt was found. In this case, the restoration of C was faster with the addition of Rose Bengal.

5 EXAMPLE V

The following two compositions were applied to an original paper of 80 microns in thickness to be 15 microns:

Composition G

	Part by weight
Photoconductive zinc oxide	100
Polybutyl methacrylate	10
Aluminum stearate	0.8
Silicone resin varnish (non-volatile 60%)	21
Sulfonamide resin varnish (non-volatile 50%)	10
Ethyl acetate	20
Toluene	20

Composition H

Composition G was mixed with 2 parts by weight of cupric sulfide.

The characteristics measured:

	G	H
Initial surface potential (volt)	300-320	280-300
Half time for dark attenuation (min.)	1	2
Relative sensitivity for xenon light source	100	120
Initial potential after pre-exposure to light of 1,000 lux from a fluorescent lamp for 5 min. and standing in a dark place for 5 min. (volt)	150-160	240-260

EXAMPLE VI

The following compositions were prepared by mixing the following ingredients respectively:

Composition I (control)

	Part by weight
Photoconductive zinc oxide	100
Silicone resin varnish (non-volatile 60%)	18
Styrene-modified alkyd resin varnish (non-volatile 50%)	32
Toluene	10
Methyl ethyl ketone	10

Composition J

Composition I was mixed with 0.4 part by weight of cupric stearate.

Each of the above coating liquid compositions I and J was coated on a shot-blasted steel plate, respectively, to form a photoconductive layer in a dried thickness of 15-18 μ . The properties of the layers are shown in the following table, wherein terms 1, 2 and 3 are the results obtained by measuring after placing in dark chamber for more than 10 hours. Further, in the preservative stability of the coating liquid in term 5, symbol "a" is the case where almost no caking is observed as a result of the precipitation of zinc oxide after allowing the coating liquid to stand in a closed vessel for more than 2 weeks and formed precipitates were easily redispersed. Symbol "b" is the case where caking was observed and the redispersion thereof was difficult.

	I	J
(1) Initial surface potential (volt)	450-500	450-500
(2) Half time for dark attenuation (min.)	5	7
(3) Relative sensitivity to xenon lamp	100	90
(4) Initial surface potential after pre-exposure in fluorescent lamp of 500 luxes for 5 min. and in dark chamber for 5 min.	100-150	420-480
(5) Preservative stability	100-150 "b"	420-480 "a"

As shown in the above table, composition I has difficulties in terms 4 and 5 whereas composition J is excellent in terms 4 and 5 as well as in other terms:

EXAMPLE VII

The following compounds were prepared:

Composition K (control)

	Part by weight
Photoconductive zinc oxide	100
Silicone resin varnish (non-volatile 60%)	35
Phenol-modified alkyd resin varnish (non-volatile 50%)	18
Toluene	20

6 Composition L

Compound K was mixed with 1 part by weight of cupric stearate.

Each of them was coated on a high-grade paper coated with substratum of polyvinyl alcohol in 60 μ thick to form a dried film of 12 μ in thickness. The results of measuring the preservative stability of the coating compositions and the characteristics of sensitive layers after drying are shown in the following table:

	K	L
(1) Initial surface potential (volt)	320-360	340-380
(2) Half time for dark attenuation (min.)	5-6	6-8
(3) Relative sensitivity to xenon lamp	100	100
(4) Initial surface potential after pre-exposure in fluorescent lamp of 2,000 luxes for 5 min. and in dark chamber for 5 min. (volt)	100-120	370-410
(5) Storage stability of liquid composition (without cobalt naphthenate)	"b"	"a"

EXAMPLE VIII

Composition M (control)

Part by weight

Photoconductive zinc oxide	100
Epoxy-modified alkyd resin (non-volatile 50%)	55

Composition N

Composition M was mixed with 0.7 part by weight of cupric stearate.

Each of compositions M and N was added with 10 parts by weight of a 10% solution of cobalt naphthenate in toluene directly before coating and then coated on a steel plate to form a dried film in a thickness of 30-35 μ . Drying was performed by allowing to stand for over night at room temperature.

The results are as follows:

	M	N
(1) Initial surface potential (volt)	450-500	450-500
(2) Half time of dark attenuation (min.)	5-6	6-8
(3) Relative sensitivity to xenon lamp	100	100
(4) Initial surface potential after pre-exposure in fluorescent lamp of 2,000 luxes for 5 min. and in dark chamber for 5 min. (volt)	100-120	370-410
(5) Storage stability of liquid composition (without cobalt naphthenate)	"b"	"a"

What is claimed is:

1. A light sensitive layer for electrophotography which consists essentially of photoconductive zinc oxide powder, an electrically insulating film-forming material, and a water insoluble cupric compound in an amount of from 0.002% to 20% of the copper ion in said compound by weight of the zinc oxide.

2. The light sensitive layer as claimed in claim 1 wherein said water-insoluble cupric compound is present predominantly in the upper 10% to 25% of the surface of the layer.

3. The layer of claim 1 wherein said cupric compound is cupric stearate.

4. The layer of claim 2 wherein said cupric compound is cupric stearate.

5. A method for producing a photoconductive insulating layer comprising an intimate mixture of a photoconductive zinc oxide powder, an organic film-forming material, and a finely divided insoluble cupric compound, said mixture provided on a support, which comprises: mixing a photoconductive zinc oxide powder and a finely divided water-insoluble cupric compound selected from the group consisting of cupric sulfide,

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cupric selenide, cupric hydroxide, cupric carbonate, basic cupric carbonate, cupric phosphate, cupric arsenite, cupric oxalate, cupric oleate, and cupric stearate with a solution of the organic film-forming material, and

coating the resulting mixture onto the support, wherein the mixing ratio of the cupric compound to the photoconductive zinc oxide powder is within the range of from about 0.002:100 to 20:100.

6. A method of producing a photoconductive insulating layer as in claim 5 wherein the film-forming material is a member selected from the group consisting of alkyd resins and epoxy ester resins.

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