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PHOTOGRAPHIC MATERIAL
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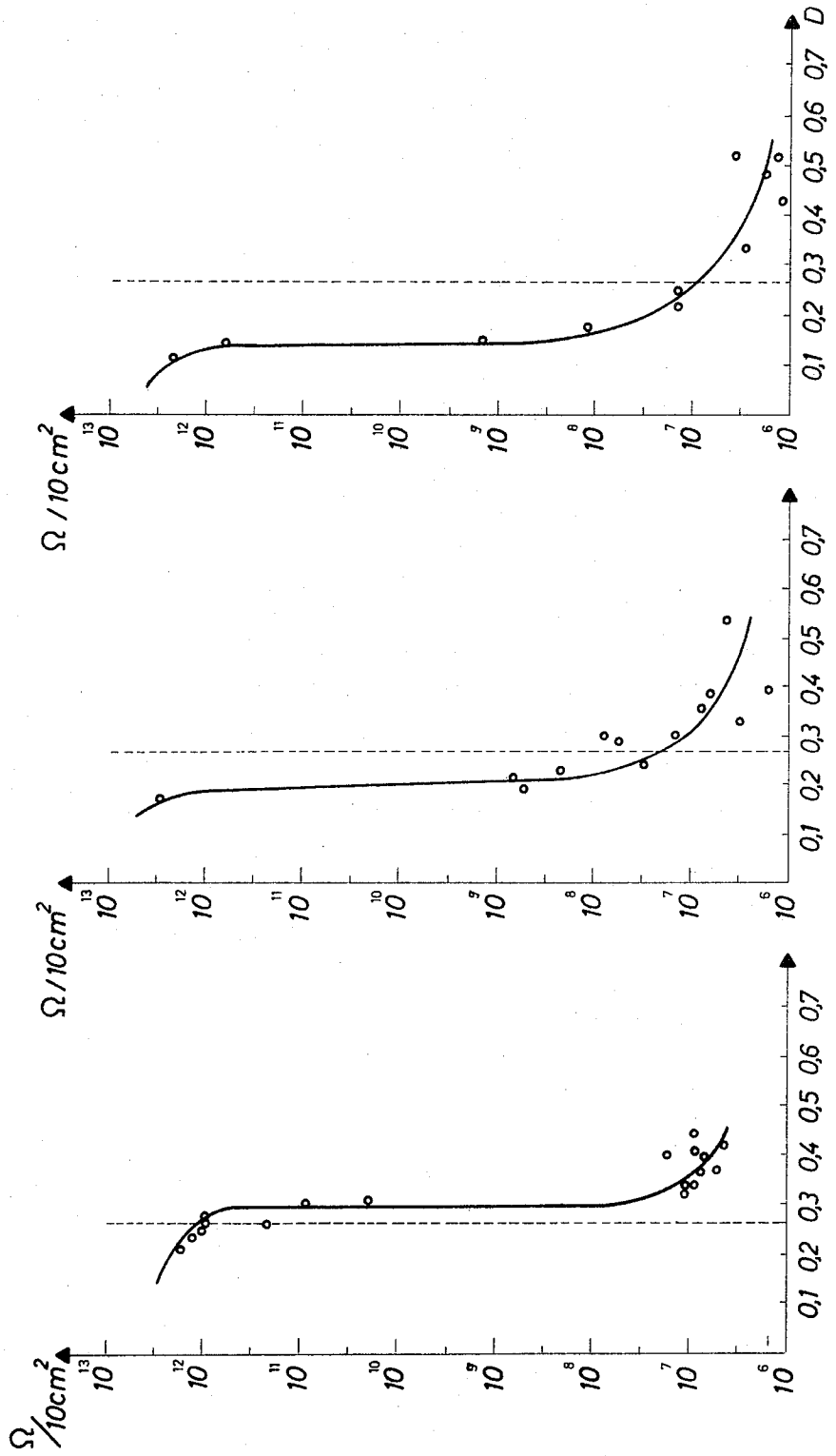


FIG. 3

FIG. 2

FIG. 1

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PHOTOGRAPHIC MATERIAL

Lodewijk Felix De Keyser, Mortsel-Antwerp, Frans Albrecht, Borgerhout-Antwerp, and Louis Achilles Meeussen, Mortsel-Antwerp, Belgium, assignors to Gevaert Photo-Producten N.V., Mortsel, Belgium, a Belgian company

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5 Claims. (Cl. 96—87)

The invention relates to a method for providing a photographic material with antistatic properties and to a photographic film material which possesses antistatic properties.

It is known that the usual film supports e.g. of cellulose acetate (di- or triacetate), cellulose nitrate or cellulose acetobutyrate possess the property of being charged electrostatically.

It is generally known that electrostatically charged films strongly attract the surrounding dust which causes a considerable dirtying of the film surface and which dust may even cause scratches. Hence, a photographic material the support of which can be electrostatically charged shows all kinds of faults which seriously interfere with film negatives of which considerable enlargements have to be made and also with films or transparencies which are destined for projection.

Moreover, on discharging a latent image of the discharge which after development becomes visible in the form of black stripes or spots, called "spark faults" is obtained in light-sensitive silver halide emulsions which are applied onto such supports.

The electrostatic charging is caused by quickly removing the film support from a material with which it is in close contact.

This can happen in the different stages of the manufacture when the film support or light-sensitive film is rolled or unrolled e.g. when the films run over the rollers of the coating-, cutting- or packing machine and also after the manufacture when treating the films or film strips e.g. when cinefilms run through the camera and the projector.

It is also known that the static charging of films can decrease by coating the plastic support with a conductive auxiliary layer.

It is further known that the resistivity of a poorly conductive binding agent can be decreased by adding to the binding agent in a sufficiently high concentration an electrolyte or a finely divided electrically conductive substance.

It is known from the British patent specification 309,659 and the French patent specification 635,828 and its patents of addition 33,191, 33,487 and 33,724, in the manufacture of antistatic films to coat a conductive layer of carbon onto the back-side of a photographic film.

From the British patent specification 544,006 a photographic film is known the support of which is coated at the back-side with a layer consisting of a dispersion of carbon in a colloidal binding agent which is insoluble in water but soluble in alkali or acids (e.g. in an acid fixing bath). This binding agent is e.g. a cellulose ester or a polyvinyl ester of a dicarboxylic acid and the mentioned layer can be used as an antihalation layer as well as an antistatic layer.

When using a too large amount of the low conductive binding agent for the colloidal carbon, the conductivity

of the antistatic layer decreases considerably. When applying the colloidal carbon as a backing layer without binding agent no satisfying result is obtained since the carbon is easily rubbed off and thus deposits onto the materials which come into contact with the film.

So, the ratio of colloidal carbon to binding agent must be chosen in such a way that a conductivity is obtained which is as high as possible and a dispersing and subbing power which is still permissible.

A process has now been found for preventing a photographic material, consisting of a plastic support such as a cellulose ester support and at least one gelatino silver halide emulsion layer, from being electrostatically charged comprising applying onto the plastic support a subbing layer for anchoring the support to the gelatin emulsion layer and which contains colloidal carbon and gelatin in a ratio not lower than 3:10.

The amount of colloidal carbon is preferably chosen in such a way that the surface resistivity of the subbing layer, applied on the plastic support, is less than 10^8 ohm/10 cm. 2, and that at the same time the optical density amounts to not higher than 0.27. In this way the constructive subbing layer functions also as an antihalation layer. The grain size of the colloidal carbon is preferably not higher than 0.05μ.

A photographic light-sensitive material according to the invention preferably consists of a transparent plastic support, e.g. a support of cellulose triacetate and at least one light-sensitive silver halide emulsion layer which is directely coated onto the antistatic gelatin containing carbon subbing layer. The colloidal carbon in the gelatin containing subbing layer preferably forms an uniform light-absorbing back-ground with a maximum optical density of 0.27.

The conductive subbing layer is much more conductive than the photographic silver halide emulsion layer so that no spark faults can arise in the emulsion and that the film moreover remains conductive even after processing.

The subbing layer preferably contains 30 to 70% of carbon by weight of gelatin. Gelatins with high ($\pm$9) as well as with low isoelectric point ($\pm$4.8) can be used.

The conductive subbing layer is coated from a dispersion of colloidal carbon in a mixture of gelatin, water and water-soluble organic solvents, such as methanol, ethanol and acetone.

In order to prevent the gelatin from flocculating in said organic solvents, an acid such as maleic acid, p-toluene sulfonic acid or nitric acid is used as dispersing agent. The quantity of water in the dispersion preferably amounts to not higher than 20%.

The colloidal carbon is dispersed in the best way by using an apparatus known in the dispersion technique such as a rapid stirrer, a homogeniser or a supersonic vibrator.

The types of carbon which are preferably used are Carbon Black TC 10 N, the trade name of Bleu d'Outremer et Couleurs de Mont St. Amand, S.A., St. Amandsberg, Belgium for its colloidal carbon, Roet "810" the trade name of Lummersheim, Germany, for its colloidal carbon and Ketjen Black ISAF, marketed by Ketjen Carbon, Amsterdam, Netherlands, for its colloidal carbon. The size of the colloidal carbon particles amounts to about 0.04μ.

The coating dispersion of carbon in gelatin is obtained as follows:

The carbon black is moistened with ethanol and while strongly stirring dispersed in this solvent. While slowly stirring this dispersion is then poured into a 10% aqueous

solution of gelatin containing an acid dispersing agent such as maleic acid. Then after strongly stirring for a sufficiently long time, the dispersion is mixed with the required amounts of water and organic solvents (ethanol/acetone or methanol/acetone). This dispersion still contains too many carbon particles which after being poured are visible because of their size. When treating the dispersion four times in a homogenizer, the degree of dispersion is improved in such a way that no visible grains can be seen anymore.

When the dispersion has to be diluted before coating because the optical density is too high, this is preferably carried out after homogenizing. Occasional coarse grained deposits in the subbing layer are due to the coagulation of many particles. Apparently the amount of water in the dispersion has an unfavourable influence.

When wetting agents such as ZELECNK (trade name of E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A., for its anionic alcohol phosphate wetting agent) are added a better contact of the support by the subbing layer and a better dispersion of the carbon particles are obtained.

For obtaining a subbing layer with an optical density of 0.27 the ratio of carbon black to gelatin may not be smaller than 3:10 otherwise the resistivity of the layer remains too high.

In order to illustrate the influence of the ratio of carbon black to gelatin on the resistivity of the layer the results of some tests are given in the curves 1, 2 and 3 of the enclosed graph.

Curve **1** shows the graphic course of the surface resistivity (Ω/10 sq. cm.) as a function of the optical density (D) of a material consisting of a transparent cellulose triacetate support coated with subbing layers of increasing thickness from a suspension comprising colloidal carbon black (grain size of about 0.04μ) in an amount of 22% by weight of gelatin.

Curve **2** shows the graphic course of the surface resistivity (Ω/10 sq. cm.) as a function of the optical density (D) of a material consisting of a cellulose triacetate support coated with subbing layers from a suspension comprsing colloidal carbon black (grain size about 0.04μ) in an amount of 37% by weight of gelatin.

Curve **3** shows the graphic course of the surface resistivity (Ω/10 sq. cm.) as a function of the optical density (D) of a material consisting of a cellulose triacetate support coated with subbing layers from a suspension comprising colloidal carbon black (grain size about 0.04μ) in an amount of 52% by weight of gelatin.

The optical density (D) is expressed with regard to a cellulose triacetate support without a gelatino carbon black subbing layer.

As appears from the three curves there exists for the optical density 0.27, an admissable minimum concentration of colloidal carbon for a resistivity decrease to 10^8 to 10^7 Ω/10 sq. cm.

It appears that this minimum concentration of colloidal carbon may be not less than 30% by weight of gelatin.

From the course of the curves it can be seen that, when following the curves from a higher to a lower optical density, a considerable increase of the resistivity is obtained at a determined optical density so that it has to be assumed that the separation between the carbon particles is too large in order to allow an electric charge to flow from one carbon particle to an other.

The theoretical lowest concentration of carbon for a minimum resistivity is the concentration whereby the carbon grains which are in electric contact with each other form a layer of a thickness of at most one grain.

The surface resitivity is measured at a relative humidity of 50% by means of electrodes of conductive rubber. The electrodes are put under a direct tension of 100 v.; they have a length of 10 cm. and a thickness of 2 mm. and are placed on the surface of the subbing layer at a distance of 1 cm. from each other. The surface resistivity is given in Ω/10 sq. cm.

The subbing layer according to the invention contains preferably 10 g. of gelatin and 5 g. of carbon per liter of suspension ready for being coated. After drying the thickness of the layer amounts to about 0.15μ.

The following examples illustrate the invention:

Example 1

15 g. of Carbon Black TC 10 N (trade name) are suspended with rapid stirring for 5 min. in 500 cm.^{3} of ethanol.

50 g. of gelatin are dissolved in 500 cm.^{3} of water at 50° C. whereupon 20 cm.^{3} of a 25% aqueous solution of maleic acid is added. The suspension of carbon black in ethanol is added to the gelatin solution while stirring and then homogenized for 20 min. with the apparatus for rapid stirring.

Then 200 cm.^{3} of the obtained suspension are diluted with 100 cm.^{3} of water, 150 cm.^{3} of ethanol and 550 cm.^{3} of acetone. This diluted suspension is four times homogenized in order to divide up the coarse carbon particles.

This homogenized suspension is then applied on a cellulose triacetate support in such a way that the formed subbing layer possesses an optical density of 0.275 (the optical density is determined with light having a wave length of 620 mμ).

The surface resistivity of this subbing layer amounts to 0.005×10^{10} Ω/10 sq. cm. A silver halide emulsion layer adheres quite well to this subbing layer in wet as well as in dry condition. In order to obtain comparative results a same subbing layer is coated containing, however, no carbon black. This subbing layer has a surface resistivity of 400×10^{10} Ω/10 sq. cm.

Example 2

A suspension of carbon black as described in Example 1 is prepared but with 35 g. of Carbon Black TC 10 N instead of only 15 g. After homogenizing, the suspension is centrifuged in order to separate the course particles. The suspension is then coated onto a cellulose triacetate support in such a way that the optical density amounts 0.247. The surface resistivity of the dried layer amounts to 0.0012×10^{10} Ω/10 sq. cm.

Example 3

The first example is repeated using, however, 25 g. of "Roet 810" (trade name) instead of 15 g. of Carbon Black TC 10 N (trade name). By diluting with ethanol and acetone before coating, the required optical density is obtained.

After coating a cellulose triacetate support with the subbing layer, the optical denisty amounts to 0.402.

The resistivity amounts to 0.00015×10^{10} Ω/10 sq. cm.

Example 4

The first example is repeated using 15 g. of Ketjen Black ISAF (trade name) instead of 15 g. of Carbon Black TC 10 N (trade name). In order to obtain the required optical density the suspension is diluted with ethanol and acetone before coating. The obtained subbing layer possesses an optical density of 0.327. The resistivity amounts to 0.0015×10^{10} Ω/sq. cm.

What we claim is:

1. Method for preventing photographic materials, consisting of a plastic support and at least one gelatino silver halide emulsion layer, from being electrostatically charged, comprising applying onto the plastic support a subbing layer for anchoring the support to the gelatin emulsion layer, said subbing layer containing colloidal carbon and gelatin, said carbon being present in an amount equal to about 30–70 percent by weight of gelatin.

2. Method according to claim 1 characterized thereby that the subbing layer has an optical density not higher than 0.27.

3. Method according to claim 1, characterized thereby that the grain size of the colloidal carbon is about 0.05μ.

4. Method according to claim 1 wherein said subbing layer is applied onto the plastic support from a dispersion containing colloidal carbon in a solution of gelatin, an acid dispersing agent, an organic solvent miscible with water and at most 20% of water.

5. Photographic material having between a cellulose ester support a gelatino silver halide emulsion layer a subbing layer of about 0.15μ thickness, said subbing layer containing gelatin and from 30% to 70% of colloidal carbon by weight of said gelatin.

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NORMAN G. TORCHIN, *Primary Examiner.*

R. L. STONE, R. H. SMITH, *Assistant Examiners.*