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3,022,169

MATTING OF PHOTOGRAPHIC LAYERS

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The present invention relates to photographic materials which contain polycarbonates as matting agents.

It is known to apply inorganic and also organic substances in finely divided form to photographic layers, especially silver halide emulsion layers, for the purpose of providing the layers with matted surfaces. Examples of substances which have been used for this purpose are barium sulphate, silica gel, kaolin, starch and waxes. These substances, however, are deposited comparatively quickly during the casting of the layers and this results in an incomplete matting effect.

It has also been proposed to use finely divided cellulose or a derivative thereof as a matting agent. In this case, however, it is essential that the cellulose or derivative thereof is comminuted to the required grain size, either by mechanical or chemical means, prior to application to the photographic layer and this involves tedious additional measures.

It has also been proposed to apply alcoholic shellac solutions to photographic layers, for the purpose of providing the layers with a matted surface. In this method, however, the shellac easily flocculates and hence it is extremely difficult to keep the size of the shellac particles within the necessary critical limits.

According to another proposal an aqueous suspension of polystyrene or polyfluorethylene is incorporated into photographic layers for the purpose of providing the layers with matted surfaces. This proposal, however, suffers from the disadvantage that particles of organic compounds frequently change in size during the drying process or on storage.

It is known that the nature of the surfaces of photographic layers plays a decisive part in the processing of most photographic films. Smooth surfaces frequently lead to contact errors and consequently to the formation of Newton's rings, especially on magnification or projection when two smooth surfaces come into contact with each other. Other disadvantages of the surfaces of photographic layers being too smooth are that the possibility of retouching the layers is poor and the layers are too sensitive to scratches.

The majority of the matting agents so far proposed have too coarse a grain size and consequently result in undesirable clouding on the surface of the photographic layer to which they are applied or show a broken line when retouching of the layer is carried out.

Prior to the present invention no means were known which prevented the formation of Newton's rings without producing an undesirable matting effect.

It has now been found that the aforementioned disadvantages in connection with the provision of matted surfaces on photographic layers can be obviated if emulsions or dispersions of polycarbonates are added either to the casting solutions employed in the production of the photographic silver halide emulsion layers themselves or to the auxiliary layers, for example the conventional protective gelatine layers.

Particularly preferred polycarbonates are those derived from di-(monohydroxyaryl)-alkanes, especially those derived from 4,4' - di - (monohydroxyaryl) - alkanes. These polycarbonates may be prepared by the processes disclosed in British patent specification No. 772,627 and

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French patent specification No. 1,141,261. Polycarbonates derived from dihydroxydiaryl sulphones or from mixtures of dihydroxydiaryl sulphones with other difunctional hydroxy compounds, such as those obtained by the process disclosed in French patent specification No. 1,152,155, are also suitable.

High molecular weight polycarbonates derived from dihydroxydiaryl ethers or dihydroxydiaryl thioethers or from mixtures of one or more of these compounds with other dihydroxy compounds are also suitable for employment in the process of the present invention. These high molecular weight polycarbonates can be prepared by the process disclosed in French patent specification No. 1,182,708.

Suitable dihydroxydiaryl ethers are 4,4'-dihydroxydiphenyl ether, 4,4'-dihydroxy-2,2'-dimethyl diphenyl ether and 4,4'-dihydroxy-3,3'-dimethyldiphenyl ether and homologues thereof.

In the dihydroxy compounds the two aryl radicals may be either the same or different and may carry substituents which will not react during the conversion of the dihydroxy compounds into the corresponding polycarbonates, for example halogen (chlorine, bromine, fluorine) alkyl groups, such as methyl, ethyl, propyl or tertiarybutyl groups or alkoxy groups.

The following substances may be used as layer formers: albumins such as gelatine and derivatives and mixtures thereof, polyvinyl alcohols, partially acetylated polyvinyl alcohols, methyl cellulose, salts of alginic acid, salts of polyacrylic acid, salts of copolymers of vinyl acetate and maleic acid and polyvinyl ethers such as polyvinylalkyl ethers, the alkyl groups of which have 1 to 12 carbon atoms.

The grain size of the matting is controlled by suitable choice of solvent and concentration of polycarbonate emulsion or dispersion. If, for example, emulsified paraffin oil is incorporated into a polycarbonate emulsion or if a polycarbonate and paraffin oil are simultaneously emulsified, it is possible to obtain a surface layer which guarantees an absolutely uniform retouching stroke. The particle size of the polycarbonate matting agent amounts to about 0.1 to 5 microns.

Other properties of the film can also be favourably influenced by incorporating a polycarbonate emulsion into gelatine layers. In this way it is possible to improve considerably the adhesion of the film to the support, the brittleness of the prepared film, the tension of the smooth layers applied to the support, the flat position of the film and also the wettability of the layers during development and the other processing steps and the strength of the film surface. The degree of matting of the resulting layer can be considerably reduced by the addition of a polyvinyl ether.

By applying a solution of a polycarbonate in a suitable solvent such as methylene chloride to which has been added one or more liquids in which the polycarbonate is insoluble or only sparingly soluble, to a smooth support such as Celluloid or glass or to gelatine or gelatino silver halide emulsion layers, there is obtained on the support after the evaporation of the solvent a surface which, with little visible matting, does not produce any disturbing Newton's rings when brought into contact with another smooth surface. If desired, other film-forming agents, such as acetyl cellulose, may be added to the polycarbonate solution. In this embodiment of the invention on evaporation of the liquid components of the polycarbonate solution the polycarbonate is precipitated on the support in a finely divided form and thus produces a finely matted surface on completion of drying. Such a modified surface can, for example, be used to improve the known regeneration of the surface with cinefilm or to remove from miniature films the tendency to form

Newton's rings on the glass plates of the diapositive frames during projection.

In order that the invention may be more clearly understood the following examples are given by way of illustration only:

Example 1

100 cc. of a 3 percent solution of a polycarbonate (such as the polycarbonic acid ester of 4,4'-di(hydroxy-phenyl)dimethylmethane) in methylene chloride is incorporated at a temperature of 35° C. and with stirring into 1 litre of a 10 percent gelatine solution to which have been added one or more wetting agents and the mixed solution is emulsified in a suitable apparatus with 100 cc. of a solution of liquid paraffin in isopropyl alcohol (1:4). After evaporating the methylene chloride, the emulsion can be used as an additive for solutions intended to be cast into photographic layers. The resulting surface formed after solidification prevents the formation of Newton's rings on contact with smooth surfaces and has excellent retouching capacity. In addition, the surface is characterised by improved wettability. Moreover, a more rapid development of the corresponding photographic layer is possible.

Example 2

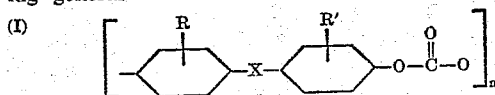
A mixture of 1 litre of a 10 percent gelatine solution to which has been added a wetting agent and 100 cc. of a 3 percent solution of a polycarbonate (such as the polycarbonate of Example 1) in methylene chloride is emulsified at 32° C. with 15 cc. of a 10 percent aqueous solution of a polyvinylether such as polyvinylmethylether, polyvinylethylether, polyvinylisobutylether, polyvinyldecylether. On adding this emulsion to gelatine or emulsion layers there is formed a surface which is very insensitive to scratching and the developed film maintains almost complete clarity. The proportion of polyvinylether to polycarbonate may vary from 10 to 100 g., and preferably 15 to 50 g. of polyvinylether per 100 g. of polycarbonate.

Example 3

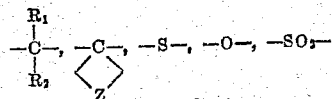
A mixture of
8 cc. of a 3 percent-solution of a polycarbonate in methylene chloride
165 cc. of methylene chloride
30 cc. of a 5 percent solution of acetyl cellulose in methylene chloride, and
95 cc. of toluene

is applied as a thin layer to a glass plate and to both sides of a developed miniature film and then dried. The glass plate thus treated in contact with a strip of normal color miniature film prevents the formation of disturbing Newton's rings on projection. The treated miniature film no longer produced any disturbing Newton's rings during projection when in contact with normal glass plates.

The present film-forming thermoplastic polycarbonates may be represented by way of example by the following general formula:



wherein X stands for a bivalent substituent selected from the group consisting of



in which substituents R₁ and R₂ stand for hydrogen, unbranched and branched monovalent aliphatic hydrocarbon radicals having 1 to 10 carbon atoms, monovalent cycloaliphatic radicals, monovalent araliphatic radicals, the alkyl groups of which contain 1 to 4 carbon atoms,

Z stands for hydrocarbon groups necessary to complete a cycloaliphatic ring; n stands for a whole number greater than 10 and preferably greater than 20; R and R' stand for hydrogen or at least one substituent which does not take part in the polyesterification process such as lower alkyl groups, alkoxy groups, halogen atoms.

The mixed polycarbonates may contain the units represented by the above general formula and by the formulae:



in which R'' stands for a phenylene radical and R''' for any bivalent radical which is different from R'' and from the corresponding radicals of the first general formula, said bivalent radical being derived from a dihydroxy compound by subtraction of the two hydroxy groups, said two hydroxy groups being the sole groups capable of taking part in the polyesterification process. These mixed polycarbonates may either contain the radicals of the Formula I and of the Formula II or of the Formula I and the Formula III or of the Formula II and of the Formula III or of all three groups. In other words the mixed polycarbonates always contain units in which the



group is bonded to an aromatic radical, said units being present in an amount corresponding to 20 to 99 molar percent.

The polycarbonates may also be produced by the processes indicated in British patent specification 772,627, French patent specifications 1,149,261, 1,152,155, 1,152,156, 1,152,157, 1,152,158 and Belgian patent specifications 546,375 and 555,894.

The paraffin oils used for the production of the matted layers in addition to said polycarbonates may contain 10 to 25, preferably 15 to 22 carbon atoms. These paraffin oils may be applied in quantities of 20 to 200 g., and preferably 50 to 150 g., per 100 g. of polycarbonate.

What is claimed is:

1. A light-sensitive photographic material comprising in combination a support, a light-sensitive silver halide emulsion layer and particles 0.1 to 5 microns in size of a thermoplastic linear polycarbonate of a dihydric phenol dispersed in a hydrophilic binding layer, said polycarbonate having a linear chain length of more than 10 carbonate units and the particles being present in amount that forms a matte surface on the binding layer.
2. A light-sensitive photographic material according to claim 1, wherein said polycarbonate particles are incorporated in said silver halide emulsion layer.
3. A light-sensitive photographic material according to claim 1, wherein said polycarbonate particles are incorporated in a protective layer coated on said silver halide emulsion layer.
4. A light-sensitive photographic material according to claim 1, wherein said polycarbonate containing layer is coated on one face of said support, and said silver halide emulsion is coated on the opposite face.
5. A light-sensitive photographic material according to claim 1, wherein a paraffin oil is dispersed in the hydrophilic binding layer along with the polycarbonate particles and the paraffin oil is present in an amount of about 20 to 200 g. per 100 g. of polycarbonate.
6. A light-sensitive photographic material according to claim 1, wherein the hydrophilic layer that contains said polycarbonate also includes a poly-vinyl alkyl ether in an amount of 10 to 100 g. per 100 g. of polycarbonate the alkyl groups of said poly-ether having up to 12 carbon atoms.

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7. A light-sensitive photographic material according to claim 1, wherein said thermoplastic linear polycarbonate is a polycarbonic acid ester of a bis-(para-monohydroxy-aryl)alkane.

8. A photographic material comprising in combination a support, a layer containing a silver image and a layer of particles 0.1 to 5 microns in size of a thermoplastic linear polycarbonate of a dihydric phenol dispersed in a hydrophilic binding layer, said polycarbonate having a linear chain length of more than 10 carbonate units, and the particles being present in amount that forms a matte surface on the binding layer.

9. A process for providing a matte photographic surface, said process including the steps of providing a solution of a thermoplastic linear polycarbonate of a dihydric phenol having a linear chain length of more than 10 carbonate units, said polycarbonate being dissolved in

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a solution which is a mixture of components one of which is more volatile and by itself effectively dissolves the polycarbonate and another of which is less volatile and by itself does not effectively dissolve the polycarbonate, applying the above polycarbonate solution on a support and evaporating off the volatile components to cause the polycarbonate to precipitate out and be deposited on the support in fine particles that provide the desired matte surface.

References Cited in the file of this patent

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