

ALIEN PROPERTY CUSTODIAN

PRODUCTION OF LIGHT SENSITIVE PHOTOGRAPHIC MATERIAL

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This invention relates to the production of light sensitive photographic material.

Light sensitive photographic material like plates, films, diazo printing foils substantially consists of a support and a light sensitive emulsion layer, mostly composed of proteins, especially gelatin, albumins etc. To use proteins for the production of the support is impossible on account of their high water sensitivity and insufficient mechanical strength. Nor are suitable hardened gelatin foils which are less water-sensitive and mechanically stronger than unhardened ones. They are for instance not flexible enough to be employed for motion picture films. On the other hand a light sensitive gelatin layer of greater thickness and possessing the necessary mechanical strength, would not be suitable for photographic purposes, as light sensitive layers surpassing a certain diameter give blurred pictures of insufficient definition because the light sensitive particles are no more lying in practically one plane.

It has been tried therefore to incorporate light sensitive compounds of organic or inorganic nature directly to the transparent or non-transparent support. These foils, however, are very sensitive towards moisture and not fast to shrinkage. Films from cellulose derivatives showing better water repellent qualities, for instance nitrocellulose or highly acetylated cellulose, cannot directly be charged with light sensitive compounds.

It is therefore the principle object of the present invention to provide a method for the production of light sensitive photographic material to be charged with light sensitive photographic compounds directly and without the application of a binding agent.

A further object is to provide a method for the manufacture of light sensitive photographic material of the described properties being fast to shrinkage and moisture-proof.

Still another object is the provision of a photographic light sensitive material consisting of superpolyamides to be charged directly with light sensitive compounds without a special binding agent like gelatin, albumin etc.

Still further objects will become apparent from the detailed specification following hereinafter.

It has been found that sheets, foils and fabrics made from superpolyamides, i. e. high molecular condensation products resembling polypeptides, obtained for instance from diamines and dicarbonic acids and their salts or from amino carbonic acids and their lactams, may be easily

charged with light sensitive inorganic and organic compounds without the use of an additional binding agent. Light sensitive compounds precipitable or adsorbable from aqueous solutions may be easily incorporated into the surface of films and filaments produced from superpolyamides or may be precipitated on them. The mechanical strength will not be weakened thereby and the exact measures of the registered images will be preserved. It is practical to use stretched, highly oriented sheets, foils and fabrics made of stretched filaments. It is also possible to first incorporate the light sensitive compounds into the sheets and foils consisting of superpolyamides and then to stretch them. These stretched foils are also suitable as optical polarizers. For that purpose it is practical to dye them with dichroitic or substantive cotton dyestuffs before or after the stretching which causes crystal orientation like Kongo Red, Cellulose Rayon Black etc.

The superpolyamides chemically related to the proteins combine in themselves, so to speak, the properties of the support hitherto used and of the well-known binding agents for the light sensitive compounds. Not inflammable, mechanically excellent single-layer motion picture films are obtained in this way as well as printing foils fast to tear and shrinkage. A wide variation is possible in the selection of the light sensitive compounds. It is possible to apply silver halide salts usual in photography, furthermore chromium and iron salts for chemographic and heliographic processes and also light sensitive organic dyestuffs and their intermediate reaction products, for instance diazo compounds of p-diamines, like N-phenyl-p-phenylene diamine or p-N-dialkylaminoaniline. The superpolyamides absorb in an excellent way dyestuffs from aqueous solutions and suspensions, so that different dyestuff classes, even sensitizers, may be applied. Most suitable are dyestuffs which are to be dyed in an acid or neutral bath and developed by an after-treatment with complex- and salt-forming means or fixed in any other way. Superpolyamide foils and fabrics may also be charged with diazo compounds which by coupling with suitable components are rendered fast to light. Finally also leuco-sulfuric acid esters of vat dyes and polymethine dyes may be used as sensitizers.

To charge the surfaces with light sensitive compounds, may be accomplished by a printing process, as for instance in cloth printing.

For the production of non-transparent photographic foils titanium white or other pigments

may be added to the superpolyamide used in the production of the foils, so that in the following printing process images on a white or bright colored back-ground are formed. Large sheets and foils consisting of superpolyamides may thus be provided in a photographic manner with any pattern desired, for instance with a wood- or marble design.

Furthermore laminated sheets and foils and fabrics may be built up of various superpolyamides in different stages of condensation in such a way, that the uppermost layer is made more capable of swelling, for instance in water, aqueous solutions and organic solvents than the middle layer. After introducing the light sensitive compounds the increased swelling properties may be wholly or partly neutralized by an after-treatment, for instance by hardening agents or the effect of heat.

Example I

A foil consisting of the polymerisate of ϵ -aminocaprolactam is bathed 5 minutes in a 5 perc. silver nitrate solution and after short washing again bathed 5 minutes in 5 perc. potassium bromide. After drying this material can be printed and developed like ordinary photographic material and the silver image obtained plays the same rôle as silver has hitherto done in the ordinary photographic materials, chemically and physically, as final image and as intermediate image, for instance in the transitory stage of the color develop process, silver bleaching process, residual image and antidiazotate process. Such material may also be worked up according to the reversal process.

Example II

A foil consisting of the polymerisate of ϵ -aminocaprolactam and containing a white pigment, for instance bariumsulfate or titanium dioxide is bathed 5 minutes in a solution of 5 perc. potassium bromide and after short washing again 5 minutes in 5 perc. silver nitrate solution. After drying the foils thus obtained may be printed like P. O. P. and may be fixed in the usual way.

Example III

A foil consisting of the condensation product of hexamethylenetetramine and adipic acid is bathed 3-5 minutes in a 4 perc. ammonium bichromate solution if necessary with addition of a softener and dried again. The layers thus obtained are exposed under a negative and yield, after etching with formic acid, reliefs suitable for pinatype- and other printing processes.

Example IV

Three foils consisting of the interpolymerisate of ϵ -aminocaprolactam and p-aminobenzoic acid are dyed by imbibition each in one of the three primary colors for subtractive color reproduction and afterwards bichromatized according to Example II. By etching, as described in Example II, colored reliefs are produced and by superimposing these three reliefs in neutral colors are obtained.

Example V

One or several dyestuffs suitable for the color bleaching process, for instance erythrosine, auramine and methylene blue, if necessary together with a chemical sensitizer like thiosinamine are incorporated by imbibition into a foil consisting of the polymerisate of ϵ -aminocaprolactam. The color images obtained in the usual way by bleaching and fixing may be used as multicolor transparencies or as prints after having been united with a light reflecting support.

Example VI

A foil consisting of the condensation product of hexamethylenetetramine and adipic acid is soaked in a solution of 4 grams of the sodium salt of the sulfuric acid ester of leuco-4,4'-dichloro-5,5'-dibromindigo, 4 grams cupferron (N-nitrosophenyl-hydroxylamine ammonium), 20 cc. glycerol and 80 cc. water and afterwards dried. The vat dyestuff forms on the exposed places during exposure.

For photography in natural colors the leuco compounds of a yellow, a purple and a blue-green dyestuff are employed in separate foils.

Fixing is done by bathing 5 minutes in warm water at 70° C.

Example VII

A foil of the condensation product of hexamethylenetetramine and adipic acid is soaked in a light sensitive solution consisting of 2.14.-diazonaphtholsulfo acid, resorcin and nickel sulfate. This foil is dried. After exposure under a matrix development with ammonia takes place in the usual way.

For protection against damaging the foils may be coated after drying prior to exposure or after development with a lacquer containing besides a cellulose ester and -ether a natural or synthetic resin and, if necessary, water-repellent substances like paraffin and softeners.

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