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# TRANSPARENT INTENSIFIER FOILS FOR USE WITH PHOTOGRAPHIC MATERIALS FOR RECORDING X-RAYS, γ-RAYS OR CORPUSCULAR RAYS

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Claims priority, application Germany, Oct. 17, 1961, A 38,575
9 Claims. (Cl. 96—82)

The invention relates to transparent intensifier foils for photographic materials for recording high-energy rays, such as X-rays, γ-rays or corpuscular rays.

Intensifier foils are already known for increasing the sensitivity of photographic materials with respect to high-energy radiation (X-rays, γ-rays or corpuscular rays) when they are brought into contact with the photographic material. High-energy radiation causes these foils to emit either fluorescent light or secondary electrons to the ray-sensitive layer. Such conventional intensifier foils, for example, metal foils or fluorescent intensifier foils such as $CaWO_4$ foils are, however, not transparent. In addition, these known intensifier foils are inconvenient to handle, more especially on account of their mechanical sensitivity. The efficiency of the metal intensifier foils decreases with high energy quanta, so that very thick metal foils are required in the high energy range; other known fluorescent intensifier foils such as $CaWO_4$ foils exhibit a disadvantageous granularity on account of their content of inorganic microcrystals. In addition, it is known to add fluorescent substances to photographic cellulose ester layer supports, however, in such a case these substances serve for marking the layer support. Layer supports, to which fluorescent substances have been added, can easily be distinguished by ultra-violet radiation from other layer supports which are free from additives.

It has now surprisingly been found that by adding organic fluorescent substances to organic synthetic plastics which contain aromatic rings, a particularly strong intensifying effect occurs under irradiation with high-energy radiation. The intensifier effect of the foils according to the invention increases with rising energy of the rays. One advantage of the intensifier foils according to the invention is that they are grain-free, so that the granularity of the image is determined only by the granularity of the photographic layer. Furthermore, these intensifier foils are transparent and have no disadvantageous influence on the photographic emulsion, so that they can be used as layer support. By comparison with the hitherto usual film-foil arrangements, a photographic X-ray, γ-ray or corpuscular ray film with an intensifying layer support has essential advantages; these are more especially a simplification of the production and a simultaneous improvement in the photographic quality, in particular an increase in sensitivity which may be due to the intimate contact of the emulsion layer and the intensifying support.

The following are examples of aromatic synthetic plastics which form particularly effective intensifier foils in combination with organic fluorescent substances, polystyrene, polyesters (for example polycarbonates and polyterephthalates), polyvinyl toluene, and also polymers of diphenyl and tetraphenyl butadienes, diphenyl hexatriene and also mixtures of such synthetic plastics containing aromatic rings.

According to a preferred embodiment of the invention those film-forming high-polymers are used for the production of the foils, which are soluble in organic solvents. For it has proved that intensifying-foils for the instant purpose which are cast from organic solution of the film-forming polymer are superior as regards the intensifying effect of the fluorescent light over foils of the same polymer which are prepared by extrusion or calendering. For this reason we prefer for the instant purpose foils of polystyrene, polyvinyl toluene and polycarbonate. Suitable polycarbonates are described in British patent specifications 808,629, 853,587 and 853,588. The production of polycarbonates are disclosed in the British patent specifications 772,627, 808,485, 808,486, 808,487, 808,488, 808,490 and 809,735.



The kind respectively the chemical structure of the fluorescing compound is not especially critical for the process according to the invention and is selected according to the requirements of the particular photographic material in which the intensifying foil is to be used.

The following substances or their derivatives are suitable as organic fluorescent substances:

| | |
|---|---|
| Anthracene | Quaterphenyl |
| Phenanthrene | Di- and Tetraphenyl ethylene |
| Chrysene | Dinaphthyl ethylene |
| Fluorene | Diphenyleneoxide |
| Triphenylene | Diphenyl acetylene |
| Terphenyl | Stilbenes |
| Coumarines | Phenyl oxazoles |
| Thoophenedioxides | Phenyl oxadiazoles |
| Benzthiophenedioxides | Pyrazolines |

Fluorescing compounds are described, for example, by R. G. Sangster et al., Journal of Chemical Physics 24 (1956), 670–715 or in our German application A 38,559 VIIIc/21g.

For a photographic intensifier action, it is necessary that the spectral range of the fluorescent emission at least paritally coincides with the spectral range of high photographic sensitivity, by which are to be undrestood both the natural sensitivity of the photographic emulsion and, with optical or chemically sensitised emulsions, the additional sensitivity ranges.

The efficacy of the intensifying foil depends on the concentration of the fluorescing compound in the foil. Therefore, combinations of film-forming polymers and fluorescing substances are preferred, which allows one to incorporate as much as possible of the fluorescing substance in the foil. Generally saturated solutions of the fluorescent compound in the polymer are used. Turbid foils are not useful for the instant purpose, care has to be taken that the fluorescing compound does not precipitate during the preparation of the intensifying foils.

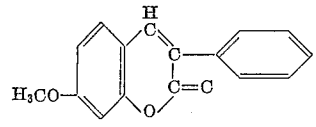
On the other side the strong intensifying effect of the aromatic polymers allows one to use foils which contain relatively small amounts of the fluorescing compounds. The concentration of the fluorescent product may be in the range of $10^{-3}$–$10^{1}$% based on the weight of the film forming polymer.

The intensifier effect of the intensifier foils according to the invention can be further improved by adding organometallic compounds or metal salts of organic acids to the organic synthetic plastic in dissolved form in quantities of advantageously 0.1 to 10% (based on the synthetic plastic) to increase the radiation absorption of the foil. As such substances having a good solubility in the organic plastic and high radiation absorption, there are considered organometallic compounds (i.e. those compounds which contain an organic group bonded directly to the metal) and metal salts of organic acids, more especially long-chain aliphatic carboxylic acids. Particularly suitable are compounds of the above type with metals of the 2nd and 4th groups of the periodic system, for example: lead and tin tetraalkyl and tetraaryl compounds, lead dialkyl, lead diaryl, tin dialkyl and tin diaryl salts of stearic, oleic, lauric and maleic acids, and also the

barium, cadmium, tin and lead salts of stearic, oleic, lauric and maleic acids. These compounds are known per se, so that they can be prepared by conventional methods. Some of the said substances are commercially obtainable, since they are generally used as stabilizers for polyvinyl chloride. Suitable compounds are, for example, described in the French patent specification 924,693 and the U.S. patent specifications 2,181,478, 2,219,463, 2,267,-779 and 2,267,778.

## EXAMPLE 1

500 g. of polystyrene (as synthetic plastic: degree of polymerisation about $10^3$ to $10^4$) are dissolved in a solution of 1 g. of a coumarine of the following formula



in 1 litre of benzene. 50 cc. of a 10% benzene solution of Ba-Cd laurate are then added to the said solution and cast to give a transparent intensifier foil with a thickness of about 0.3 mm.

This intensifier foil is used as support for a highly sensitive silver halide emulsion, which is cast in the usual way on to the foil. The sensitivity of this film is substantially higher than that of a corresponding film with a cellulose ester support containing fluorescent substances in the same concentration, as is shown by the following table:

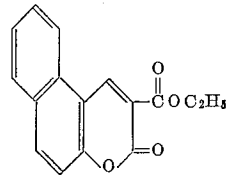
| Energy of ray source: | Increase in sensitivity |
|---|---|
| 150 kv. | By the factor 2. |
| 200 kv. | By the factor 3. |
| 300 kv. | By the factor 5. |
| 1.25 mev. | By the factor 5. |

(Measured at the density 1.)

The fluorescing compound is prepared according to Example 3 of the published German application F 30,600 IVc/8i (DAS 1,102,694).

## EXAMPLE 2

300 g. of a polycarbonate based on 2,2-(4,4'-bis-hydroxyphenyl) propane (degree of polymerisation about $10^3$ to $10^4$) are dissolved in a solution of 1 g. of ethyl 5,6-benzocoumarine-3-carboxylate



in methylene chloride, 50 cc. of a 10% methylene chloride solution of dibutyl-tin maleinate are added thereto and the mixture is cast to give a transparent foil with a thickness of about 0.5 mm. These intensifier foils are brought into contact on both sides with a highly sensitive normal commercial X-ray film. The increase in sensitivity which is achieved is substantially greater than when using a corresponding foil with a cellulose ester base.

| Energy of ray source: | Increase in sensitivity |
|---|---|
| 150 kv. | By the factor 1.5. |
| 200 kv. | By the factor 2.5. |
| 300 kv. | By the factor 3. |
| 1.25 mev. | By the factor 3. |

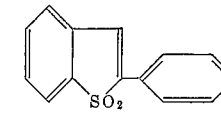
(Measured at the density 1.)

The above coumarine-derivative is described in Example 1 of the published German application F 18,533 IVc/8i (DAS 1,090,624).



## EXAMPLE 3

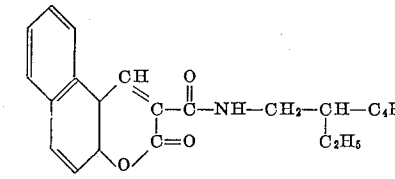
500 g. of polyvinyl toluene (degree of polymerisation about $10^3$ to $10^4$) are dissolved in a solution of 5 g. of 2-phenyl benzthiophene dioxide



in 1 litre of benzene. 50 cc. of a 10% benzene solution of dibutyl-tin dilaurate are added thereto and the mixture is then cast as a transparent intensifier foil. The fluorescing compound is described in published German application D 23,838 IVc/8i (DAS 1,063,571).

## EXAMPLE 4

250 g. of polystyrene and 250 g. of a polymer of tetraphenyl butadiene are dissolved in a soltuion of 5 g. of the following compound (prepared by reaction of the compound described in Example 2 with 2-ethyl hexylamin):



in 1 litre of benzene. 50 cc. of a 10% benzene solution of lead tetraphenyl are added to the mixture, which is cast into a transparent intensifier foil.

## EXAMPLE 5

*Production of a transparent intensifier foil*

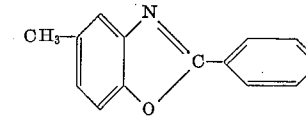
A solution of 500 g. polystyrol in 1 l. benzene is mixed with 100 ccm. of a 10% benzene solution of the fluorescing compound disclosed in Example 1. The resulting solution is cast to give an intensifier foil, having a thickness of approximately 0.3 mm.

A commercial X-ray film being highly sensitive and having a steep gradation, e.g., the film "Agfa Röntgen-Radiolix," is arranged between 2 of the intensifier foils described above, whereby the light-sensitive layers of the film are in intimate contact with said foils.

This film foil combination is exposed to X-rays of 300 kv. direct voltage and developed in a usual developer, e.g., the "Agfa-Röntgen-Rapid-Developer E60." The sensitivity of the film is increased by the factor 3, compared with the same film which is processed without intensifier foils.

## EXAMPLE 6

A mixture of 400 g. of 4,4'-dihydroxydiphenyl-dimethylmethan polycarbonate as described in Example 1 of British patent specification 808,629, in 1.5 l. methylene chloride and 200 ccm. of a 10% methylen-chloride solution of 2-phenyl-5-methyl-benzoxazol having the following formula:



is cast to give a transparent intensifier foil having a thickness of 0.2 mm. Both sides of this foil are coated with a subbing layer according to Example 2 of the British patent specification identified above. On to the subbing layers are applied light-sensitive layers of a high-sensitive silver bromide-iodide emulsion as generally used for the production of X-ray films. The light-sensitive layers have a thickness of 10$\mu$.

The film is exposed behind the material to be tested, e.g., a steel tubing with X-rays of 300 kv. The film is

developed with the usual X-ray developer, e.g., the Agfa-Röntgen-Rapid-Developer E60.

The sensitivity of the film is increased by the factor 3 compared with a film of the same type but which contains no fluorescing substances in the support. Furthermore, the contrast is considerably improved in the density range of below approximately 2.5.

The film described above can be used in combination with additional intensifier foils as described in Example 5 or with lead intensifier foils or other conventional intensifier foils known per se. The fluorescing benzoxazol derivate is prepared according to Berichte der Deutschen Chemischen Gesellschaft 31, 2696.

Photographic materials which contain the intensifier foils according to the invention are suitable for recording X-rays, $\gamma$-rays or corpuscular rays. The preferred use is on the technical field, for example, for non-destructive testing of material or as monitoring films for measuring the dosage of high-energy radiation. They are superior in many respects to the known films for these purposes and especially also to the photographic materials which contain organic fluorescent substances in the light-sensitive layer, since the addition of the intensifying additives to the emulsion layer results in a clouding and in addition a flattening of the gradation. The fluorescent light generally has wavelengths of between 200–600 m$\mu$. Most important is the light between 350–450 m$\mu$.

We claim:

**1.** A photographic material for recording high-energy radiation comprising at least one silver halide emulsion layer sensitive to said high-energy radiation and in intimate contact therewith a transparent foil of a film-forming polymer which contains benzene rings selected from the group consisting of polystyrene, polyesters, polyvinyl toluene, polydiphenyl butadienes, polytetraphenyl butadienes, polydiphenyl hexatrienes and mixtures thereof, said polymer having dissolved therein an organic fluorescent compound that converts the high-energy radiation into light having a wave length of between 200 to 600 m$\mu$.

**2.** The photographic material of claim **1** wherein at least one of the silver halide emulsion layers is coated on the foil of film-forming polymer.



**3.** The photographic material of claim **1** wherein at least one of the silver halide emulsion layers is coated on a supporting foil different from that of the film-forming polymer.

**4.** The photographic material of claim **1** wherein the film-forming polymer is polystyrene.

**5.** The photographic material of claim **1** wherein the film-forming polymer is a polycarbonate.

**6.** The photographic material of claim **1** wherein the organic fluorescent compound is selected from the group consisting of coumarines, benzthiophene dioxides and benzoxazols.

**7.** The photographic material of claim **1** wherein the film-forming polymer additionally contains dissolved therein a metal compound selected from the group consisting of organo-metallic compounds and metal salts of aliphatic carboxylic acids, the metal being selected from group consisting of the second and fourth group of the periodic system.

**8.** The photographic material of claim **7** wherein the metal compound is a tin salt of an aliphatic carboxylic acid.

**9.** The photographic material of claim **7** wherein the metal compound is an organo-tin compound.


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# UNITED STATES PATENT OFFICE

# CERTIFICATE OF CORRECTION

Patent No. 3,282,697 November 1, 1966

Rudolf Blank et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the heading to the printed specification, line 7, for "Roderich Rause" read -- Roderich Raue --; column 2, line 27, for "Thoophenedioxides" read -- Thiophenedioxides --; line 35, for "paritally" read -- partially --; line 36, for "undrestood" read -- understood --.

Signed and sealed this 5th day of September 1967.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents