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3,729,318

PROCESS FOR CROSS-LINKING SILVER HALIDE GELATINO EMULSION LAYER CONTAINING NON-DIFFUSIBLE COMPOUND HAVING EPOXIDE AND ISOCYANATE GROUPS

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U.S. Cl. 96—111 4 Claims

ABSTRACT OF THE DISCLOSURE

Photographic gelatine layers have to be hardened in order to improve the mechanical properties and to raise the melting point of the layer. Excellent hardening is obtained by means of low molecular compounds having a hardeny epoxide and a hardening isocyanate group.

The invention relates to a process for hardening layers which contain gelatin using a hardener which is fast to diffusion.

The irreversible cross-linking of the binder of photographic layers is of considerable importance because these layers are treated with various aqueous baths in the course of processing and they must therefore be highly resistant to aqueous solutions, and particularly to alkaline solutions. This is achieved by adding to the proteins which commonly are used to form the layer substances which are capable of undergoing a cross-linking reaction with the protein chains thus raising the melting point of the proteins. This reaction, however, must not reduce the permeability of the proteins to water and in many cases, e.g. in the silver salt diffusion process, it is in fact desirable that the hardened layers should be capable of rapidly taking up a large quantity of water in order to ensure rapid and complete processing.

Numerous compounds and types of compounds which may be used as hardeners for proteins have already become known. The following are given as examples:

Metal salts, such as salts of chromium, aluminium and zirconium; aldehydes and aldehyde compounds which contain halogen, e.g. formaldehydes, dialdehydes and mucochloric acid; 1,2- and 1,4-diketones such as cyclohexane-1,2-dione, quinones, chlorides of dibasic organic acids, dianhydrides of tetracarboxylic acids, and compounds which contain several reactive vinyl groups, e.g. vinyl sulfones, and arylamides; compounds which have at least two heterocyclic rings which are easily cleaved, e.g. ethylene oxide and ethylene imine, polyfunctional methane sulfonic acid esters, bis-α-chloroacylamido compounds and heterocyclic compounds which have active halogen atoms, e.g. halogeno-1,3,5-triazine compounds.

These hardeners are low molecular weight compounds. Some of them are photographically active and therefore cannot be used for certain photographic emulsions. Others, such as the metal salts, increase the brittleness of the layers. Dialdehydes and diketones discolor the layers in various ways and are therefore unusable. Furthermore, acid chlorides and acid anhydrides in many cases alter the pH of the casting solutions so that the pH would have to be readjusted with alkali, which is undesirable or may be impossible because it would impair other photographic properties. It is also known that many hardeners cause fogging or a reduction in the sensitivity of the emulsion after prolonged storage.

Other hardeners again have the disadvantage that the hardening process starts only after some time in storage so that the properties of the layers undergo uncontrollable changes. Lastly, all hardeners which are non-diffusion-fast have the disadvantage that when used in multilayered materials it is difficult to confine their activity to a particular layer.

High molecular weight hardeners have also been described, e.g. periodic oxidation products of starch, and plant gums such as tragacanth, gum arabic, alginic acid, pectins and xylans. These compounds have, however, the disadvantage that they have only a low hardening equivalent. Alginic acid esters and maleic acid half esters of high molecular weight alcohols such as polyvinyl alcohol have similar disadvantages.

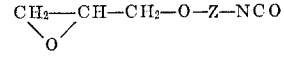
Lastly, macromolecular polymerization products of acrolein have also been proposed as hardeners, but they can only be used in the form of their water-soluble bisulfite addition compounds. This is a disadvantage because after preparing the polyacrolein it is necessary to carry out a second operation to obtain the bisulfite addition compound, and the removal of excess sulfurous acid or sulfite can only be achieved by complicated operations.

Now, as before, there is a need for diffusion-fast hardeners which can be used for producing photographic materials which contain an unhardened layer adjacent to a highly cross-linked layer. Such systems are very important for so-called stripping films. Hardeners which are not diffusion-fast naturally cannot be used for these films because the hardener become distributed throughout the whole stack of layers and all the layers would be cross-linked. Low molecular weight hardeners could in principle be rendered diffusion-fast by known methods. Thus, for example, longer alkyl radicals having more than 10 carbon atoms could be introduced. This method, however, generally leads to complete or partial loss of the hardening activity of the hardeners. Although high molecular weight hardeners are diffusion-fast, they have various other disadvantages, as already mentioned above. For example, the viscosity of their aqueous solutions is relatively high, which makes processing more difficult. Moreover, it is difficult to free high molecular weight compounds from unwanted impurities.

It is among the objects of the invention to provide low molecular weight diffusion-fast hardeners for protein layers, by means of which the hardening process can be confined to one layer within a multilayered photographic material.

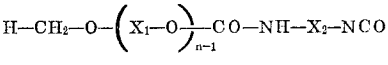
A process for hardening photographic gelatin layers by the addition of low molecular weight hardeners has now been found in which the hardeners used are compounds which contain an isocyanate group and an epoxide group.

The hardening compounds correspond, for example, to the folloming formula:

(I) 

wherein Z represents a bivalent organic linking member, preferably a branched or unbranched, saturated or ethylenically unsaturated aliphatic radical containing up to 10 carbon atoms, arylene, especially phenylene, or cycloalkylene, preferably cyclohexylene, which may be interrupted by ether (—O—), carbamoyl (—CO—NH—) or urethane (—O—CO—NH—) groups.

More particularly suitable are compounds of the following formula:

(II) 

wherein n represents the integer 1, 2 or 3, preferably 1 or 2, each of X_1 and X_2 represents a bivalent hydrocarbon group with up to 18 carbon atoms, preferably with 2 to

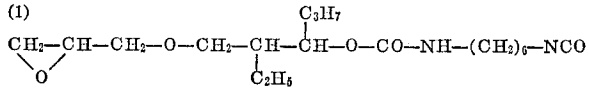
15 carbon atoms. More particularly X_1 and X_2 represent a bivalent straight-chain or branched aliphatic group, which may be saturated or olefinically unsaturated, a bivalent cycloaliphatic group such as cyclohexylene, a bivalent aromatic group such as phenylene or naphthylene. Also included are mixed hydrocarbon groups, for example combinations of aliphatic groups with aromatic or cycloaliphatic groups such as tolylene or xylylene or methylenecyclohexylene. Particularly preferred are compounds in which X_1 stands for an aliphatic group having up to 10 carbon atoms.

The compounds for use according to the invention are characterized by the isocyanate group and the epoxide ring. Both groups react with amino groups of the protein binder, e.g. gelatin, but the isocyanate group reacts much more rapidly than the epoxide group, in fact it reacts immediately when these compounds are added to the solution of protein. The hardener is thus combined in a diffusion-fast manner with the film forming agent. The epoxide group which reacts much more slowly reacts only after the layer has been produced, in the course of drying or storage of the photographic material. Herein lies the advantage of the compounds used according to the invention. The cross-linking agent is fixed by the one reactive group, but the viscosity of the protein solution is not increased. The compounds therefore behave quite differently from those which contain two isocyanate groups or two epoxide groups. Those which contain two isocyanate groups react so rapidly in aqueous solution that cross-linking and a high increase in the viscosity is even observed in the casting solutions. Compounds which have two epoxide groups react only slowly in the course of drying or storage and they are therefore not present in a diffusion-fast form in the layers.

The two functional groups of the hardeners according to this invention are connected together by the linking member Z in Formula I. The linking member due to its non-critical nature, can of course be of any structure, and accordingly the hydrocarbon groups can be substituted, for example, with alkyl which would constitute an aliphatic hydrocarbon side chain, or with alkoxy or halogen, especially chlorine. However the substituents should not impair the reaction of the epoxide or isocyanate groups with gelatin.

Compounds of the following formulae have proved to be especially suitable:

(1)



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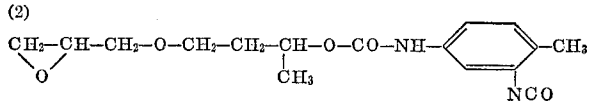

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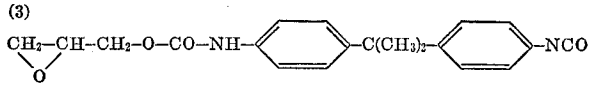

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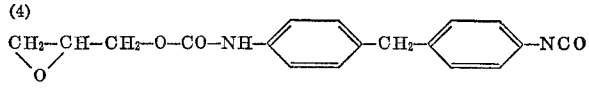

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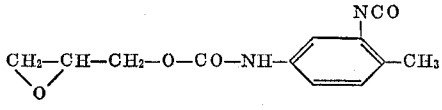

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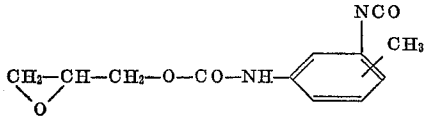

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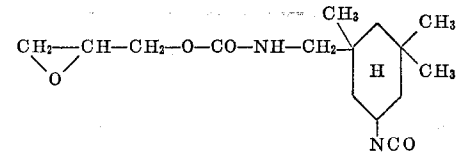

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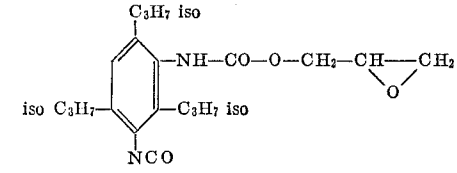

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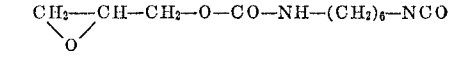

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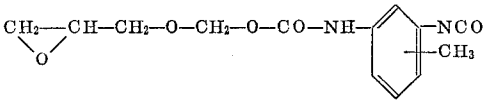

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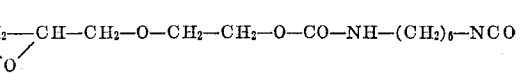

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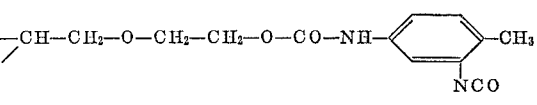

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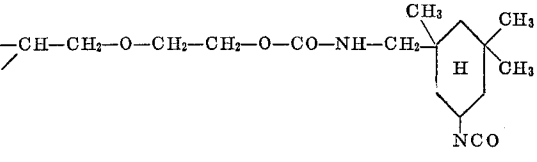

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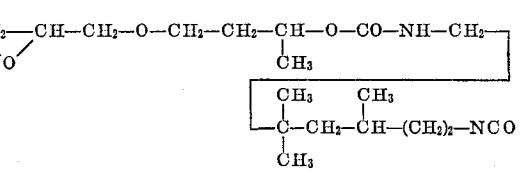

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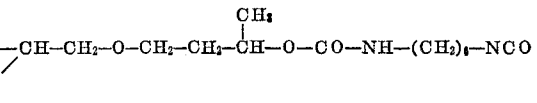

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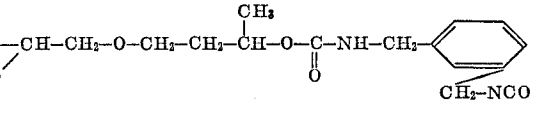

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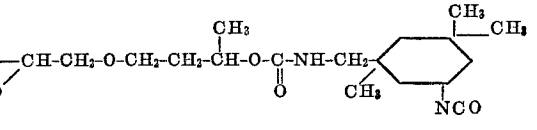


Compounds of the type mentioned above are known per se. They have been described in German patent specification No. 862,888. The preparation of some of the compounds is described in detail below and the other compounds are prepared in analogous manner.

COMPOUND 4

25 g. of diphenylmethane-4,4-diisocyanate (Desmodur-44) (0.1 mol) are dissolved in 100 ml. of xylene and heated to 100° C. and 7.4 g. of glycidol (0.1 mol) are added at this temperature. The reaction mixture is cooled

and the supernatant layer is decanted from the oil which has separated and the oil is boiled several times with petroleum ether. Yield about 30 g.

COMPOUND 5

52.2 g. (0.3 mol) of tolylene-2,4-diisocyanate (0.3 mol) in 150 ml. of clean petrol ether are heated to 100° C., 100 mg. of 1,2,4-triazole are added as a catalyst, and 22.2 g. of glycidol (0.3 mol) are the introduced dropwise with stirring. The supernatant layer is decanted while still hot from the bis-glycidyl urethane which has separated. This is then left to get cold and the crystallized product is filtered off. Yield 40–50 g.

COMPOUND 7

67 g. of isophorene diisocyanate (0.3 mol) are heated to 100° C., 22.2 g. of glycidol (0.3 mol) are added dropwise with stirring, the reaction mixture is left to get cold and the resulting viscous mass is boiled several times with petroleum ether. Yield 70 g.

COMPOUND 9

(a) A solution of 33.6 g. of hexamethylenediisocyanate in 20 g. of absolute benzene is heated to 80° C. and 7 g. of glycidol are added dropwise with stirring. The solution is then heated for one hour at 80° C. and filtered, and benzene and excess diisocyanate are removed under vacuum. A thick oil remains. Yield 35 g.

(b) 50.4 g. of hexamethylene diisocyanate (0.3 mol) are heated to 100° C., 22.2 g. of glycidol (0.3 mol) are added dropwise with stirring, the reaction mixture is left to cool and the viscous oil is boiled several times with petroleum ether. Yield 60 g.

COMPOUND 10

17.4 g. (0.1 mol) of commercial tolylene diisocyanate (approximately 80% 2,4- and 20% 2,6-tolylene diisocyanate) are heated to 100° C., 11.8 g. of ethylene glycol monoglycidyl ether are added dropwise with stirring, the reaction mixture is left to cool after 30 minutes and the oil is extracted several times with petroleum ether. Yield: 30 g. of an oil which contains substantial quantities of petroleum ether.

For the preparation of compounds for use according to the invention see also German Offenlegungsschrift No. 1,901,024 or U.S. application Ser. No. 843.

The term "photographic layers" includes quite generally any layers used for photographic materials, e.g. light sensitive silver halide emulsion layers, protective layers, filter layers, antihalation layers, backing layers or photographic auxiliary layers in general.

The effect of the compounds used according to the invention is not impaired by the usual photographic additives and the hardeners according to the invention are also inert to photographicaly active substances such as color couplers, stabilizers and sensitizers. Also, they have no influence on the light sensitive silver halide emulsions.

The compounds are preferably used in the form of their solutions in aprotic solvents in quantities of 0.5 to 8%, preferably 1 to 5% (based on the dry weight of gelatin). They are added before the gelatin solutions are cast and preferably before digestion. The solutions are then digested for at least ½ hour at 35 to 40° C. to ensure that the isocyanate groups have undergone complete reaction. This is essential to ensure that the hardener is fixed in a diffusion-fast form. The layer binder may contain other water-soluble high molecular weight compounds in addition to gelatin, e.g. polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene oxide and polyacrylamide and latices of water-insoluble high molecular weight compounds such as polyethyl acrylate, polybutylcryltae and other copolymers which serve as plasticizers or as additives which increase the covering power of silver. Casting may be followed by a prolonged period of drying before a new layer is applied. The technical advance provided by the

application of the compounds according to the invention consists in the fact that hardening is strictly confined to layer to which the hardener has been added. When building up an assembly of layers, there is no difficulty in following a strongly hardened layer with a less hardened or unhardened layer. When using conventional hardeners, the preparation of multilayered assemblies of this kind can generally only be achieved if certain precautions are taken. If, for example, a layer of unhardened gelatin which can be washed off at 36° C. is to be cast onto a layer I which has been hardened with formalin, the excess formalin must either be removed from layer I by storing the layer or tempering it at elevated tempertaures or more preferably an intermediate layer which binds the formalin must be placed between layers I and II.

The melting point of the layers is determined as follows: Half of the layer which has been cast on a support is dipped in cold water which is continuously heated by 5° C. per minute up to 100° C. The temperature at which the layer runs off the support (formation of streaks) is taken as the melting point. In other tests, the layers which had been hardened in accordance with the invention were first treated for 5 minutes with a 5% aqueous sodium carbonate solution and the melting points were then determined both immediately after drying and after the layers had been stored as indicated above. Under the conditions at which the measurement are carried out, pure gelatin layers which contain no hardener in no case showed an increase in melting point.

Example 1

5 ml. of a 5% aqueous saponin solution are added as wetting agent to 160 cc. of a 10% aqueous gelatin solution and the compounds are added in each case in amounts of 2% based on the gelatin content. The compounds are dissolved in ethyl acetate and dispersed in the gelatin. The pH of the solution is adjusted to 6.2. The casting solutions are poured on a previously prepared cellulose triacetate support. After drying, the layers (layer I) are stored for 36 hours at 57% C. and 34% relative humidity. After determination of the melting point, the cast layer is covered with a conventional silver halide gelatin emulsion without hardener, which emulsion contains 45 g. of silver halide and 60 g. of gelatin per kg. The melting point of the emulsion layer (layer II) is determined after storing for 36 hours at 57° C. and 34% relative humdity.

TABLE I

Hardener	Melting point of— Layer I, ° C.	Layer II, ° C.	Remarks
Comparison: 2% 1,3,5-N,N',N''-trisacryloylhexahydrotriazine.	100	100	
2% compound 5	>100	36	Properties remain unaffected.
2% compound 7	>100	40	
2% compound 9	>100	40	
2% compound 10	>100	40	
2% compound 16	>100	39	

The figures above show that in contrast to the triazine hardeners, the compound according to the invention are diffusion-fast, and hardening is in each case confined to the layer to which the hardener has been added.

Example 2

1%, 2% and 5%, respectively, of the compounds according to the invention dissolved in ethyl acetate solution (percentage content based on the gelatin) were added in an emulsified form to 1 kg. of a silver halide gelatin emulsion of the type conventionally used for black and white material containing per kg. 80 g. of gelatin. The solutions are left to stand for ½ hour at 36° C. and then cast on a baryta-coated paper support after the addition

of saponin as wetting agent. The melting points are determined after storage under the following conditions:

Conditions I: 48 hours' storage of the layers at room temperature with exclusion of moisture.

Condition II: 36 hours' storage of the layers at 57° C. and 35% relative humidity.

TABLE II

	Melting point of the layer in ° C.[1]		
	Condition I	Condition II	Swelling in percent
Compound 1:			
1%	50°	10'100°	495
2%	81°	10'100°	400
Compound 2:			
1%	42°	45°	
2%	46°	10'100°	540
Compound 3:			
1%	41°	44°	
2%	84°	1'100°	590
Compound 4:			
1%	59°	10'100°	360
2%	10'100°	10'100°	280
Compound 7:			
1%	50°	5'100°	590
2%	2'100°	10'100°	550
Compound 5:			
1%	62°	10'100°	520
2%	10'100°	10'100°	390
Compound 9:			
1%	42°	10'100°	
2%	10'100°	10'100°	430
Compound 10:			
1%	38°	3'100°	490
2%	50°	10'100°	420
Compound 11:			
1%	50°	10'100°	465
2%	2'100°	10'100°	390
Compound 12:			
1%	50°	10'100°	515
2%	2'100°	10'100°	360
Compound 13:			
1%	37°	2'100°	480
2%	50°	10'100°	410
Compound 14:			
1%	45°	10'100°	480
2%	100°	10'100°	390

[1] 10'100° means that the melting point of gelatin is above 100° C. and the a yer dissolves off only after 10 minutes boiling in water.

The table shows that the compounds according to the invention are efficient hardeners. They do not influence the photographic properties of the emulsion.

Swelling of the layers is determined gravimetrically after 10 minutes treatment of the layers in distilled water at 22° C. and it is indicated in percent.

Example 3

3 g. of Compound 5 and 3 g. of Compound 9, respectively, are added to 1 kg. of a silver chlorobromide emulsion which is ready for casting and which contains 60 g. of gelatin, silver halides in an amount which corresponds to 38 g. of silver nitrate and 18 g. of 1-hydroxy-4-sulfo-N-octadecyl-2-naphthamide as cyan-forming coupler. The emulsions were cast on a layer support of triacetylcellulose. Determination of the melting points of the layers and of the amount of swelling were carried out after storing the material for 36 hours at 57° C. and 34% relative humidity.

TABLE III

	Melting point	Swelling in percent, 10 min., 22° C.
5% compound 5	10'100° C	560
5% compound 9	10'100° C	400
0% hardener	36° C	>800

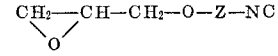
The photographic properties are not affected and the color shade of the dye is not altered.

Example 4

2% of Compound 7 (based on gelatin) are added to a 6% aqueous gelatin solution. The mixture is digested for ½ hour at 40° C. and it is cast on a previously prepared cellulose acetate support after the addition of a wetting agent. The layer is dried and kept for 36 hours at 34% relative humidity at 57° C. A layer of gelatin which does not contain hardener is then cast on the first layer. After drying, a silver halide gelatin emulsion to which 2% of Compound 7 have been added and which has also been digested for ½ hour at 40° C. is applied. After this has been kept at 34% relative humidity and 57° C. for 36 hours, the melting point of the upper and lower layer has risen to 100° C. The melting point of the middle layer is 42° C., which proves that the hardener is fast to diffusion.

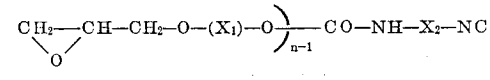
We claim:

1. In a process for the production of a photographic light sensitive element having a plurality of layers including at least one silver halide gelatino emulsion onto a layer support and drying, the improvement consisting or casting a silver halide gelatino emulsion containing an effective amount of a non-diffusible compound having the following formula:



wherein Z represents a bivalent, saturated or ethylenically unsaturated aliphatic radical containing up to 10 carbon atoms, or arylene, drying the cast layer and cross-linking said compound in the dried silver halide gelatino emulsion to yield a hardened layer.

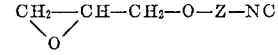
2. The process of claim 1, wherein the hardening agent has the formula



wherein n represents 1 or 2 and each of X_1 and X_2 represents a bivalent straight-chain or branched aliphatic group, which may be saturated or olefinically unsaturated, or a bivalent cycloaliphatic group.

3. The process of claim 2, wherein X_1 is an alkylene group having up to 10 carbon atoms and X_2 is (1) an alkylene group having up to 10 carbon atoms, (2) a bivalent cycloaliphatic group, (3) a phenylene group or (4) a bridge member containing alkylene and phenylene or alkylene and a bivalent cycloaliphatic group.

4. A photographic light sensitive element having a plurality of layers including at least one sliver halide gelatino emulsion layer containing an effect amount non-diffusible compound having the following formula:



wherein Z represents a bivalent, saturated or ethylenically unsaturated aliphatic radical containing up to 10 carbon atoms, or arylene, said compound being cross-linkable in the dried silver halide gelatino emulsion to yield a hardened layer.

References Cited

UNITED STATES PATENTS

3,220,864	11/1965	Kenyon et al.	96—111 X
3,047,394	7/1962	Allen et al.	96—111
3,551,159	12/1970	Froehlich	96—111
3,103,437	9/1963	Henn et al.	96—111

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U.S. Cl. X.R.

260—117; 117—34; 106—125

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,729,318 Dated April 24, 1973

Inventor(s) Wolfgang Himmelmann et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 21, "hardeny" should read -- hardening -- .
Column 1, line 52, "arylamides" should read -- acrylamides -- .
Column 2, line 29, "hardener" should read -- hardeners -- .
Column 5, line 8, "the" should read -- then -- .
Column 5, line 71, "polybutylcryltae" should read -- polybutylacrylate -- .
Column 6, line 3, before "layer" insert -- the -- .
Column 6, line 13, "tempertaures" should read -- temperatures -- .
Column 8, lines 16 and 17, after "emulsion" insert -- layer by casting the gelatino-emulsion -- ; after "consisting" the word "or" should read -- of -- .

Signed and sealed this 20th day of November 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

FORM PO-1050 (10-69)

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