United States Patent Office

3,262,781

Patented July 26, 1966

3,262,781

PHOTOGRAPHIC PRODUCTS

William H. Ryan, Carlisle, and Lloyd D. Taylor, Everett, Mass., assignors to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

No Drawing. Filed July 5, 1962, Ser. No. 207,794
6 Claims. (Cl. 96—76)

The present invention is concerned with photosensitive silver halide emulsions and more particularly with photosensitive silver halide emulsions which have silver halide developing agents disposed therein.

An object of the present invention is to provide photosensitive silver halide emulsions, having silver halide developing agents disposed therein, which are stable on storage and which after exposure can be developed by a simple treatment with an alkaline solution.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

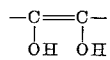
The invention accordingly comprises the product possessing the features, properties and the relation of components which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

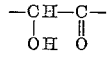
It has long been known to incorporate photographic developing agents into photosensitive silver halide emulsions so that such emulsions may be developed by means of a simple treatment with an alkaline solution. Generally, in incorporating the developers in the emulsion, it has been found necessary to place them in an inactive condition so as to prevent fogging and staining on storage.

It has been discovered, in accordance with the present invention, that good stability on storage may be achieved by forming cyclic boronic esters of the developers and disposing them in this state in the photosensitive elements. Upon treatment with alkali, after exposure the cyclic esters readily hydrolyze and the developers are free to develop the latent image.

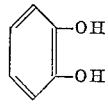
Generally, the developers which can be formed into cyclic esters are the α,β-enediol developers. According to Kendall's rule, α,β-enediol developers are compounds which contain in their molecular structure a segment having the following formula:

(A) 

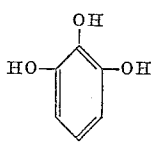
or when said segment undergoes a tautomeric shift:

(B) 

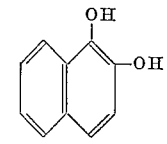
Such segments may be part of an aromatic ring such for example as in:

(1) 

catechol

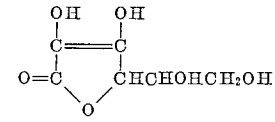
(2) 

pyrogallol

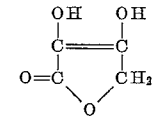
(3) 

1,2-dihydroxynaphthalene

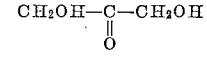
or part of an aliphatic or heterocyclic structure such for example as in:

(4) 

ascorbic acid

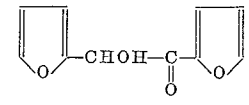
(5) 

hydroxytetronic acid

(6) 

dihydroxy acetone

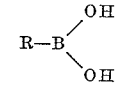
or

(7) 

furoin

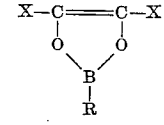
Especially useful results have been obtained using the orthodihydroxyaryl developers.

Boronic acids for use in preparing the cyclic esters are boric acid derivatives in which one of the —OH groups has been replaced by an organic radical. Generally, such acids may be represented by the formula:

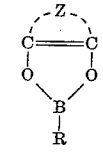


wherein R is an organic radical, e.g., an alkyl group such as an ethyl, propyl, octyl, octadecyl radical; an aralkyl group such as a benzyl radical, an aryl group such as a phenyl, naphthyl, or biphenyl radical; etc. As will be understood, R in the cyclic esters of this invention may be any organic radical because, as set forth above, it is split off by hydrolysis and does not take part in the development of the silver halide emulsions.

Cyclic esters within the present invention may be represented by the formulae:



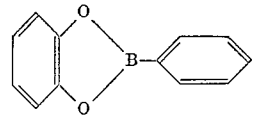
and



wherein R is an organic radical, each X is a hydrogen or alkyl radical and Z represents the atoms which complete a heterocyclic or aromatic ring.

As an example of a cyclic ester which has been found

especially useful, mention may be made of the phenylboronic acid ester of catechol, i.e.:



The photosensitive elements of the present invention may be prepared by dispersing the cyclic esters in conventionally prepared silver halide emulsions and coating the resulting dispersion on a suitable support. In a preferred method of preparing the dispersion, the cyclic esters are first dissolved in an organic solvent and then added, with stirring, to the aqueous emulsion coating solution. Usually the esters will be insoluble in the aqueous solutions and precipitate out to form a fine dispersion.

After exposure, the developers may be rendered active by treating the photosensitive element with an alkaline solution. Such alkaline solutions bring about hydrolysis of the esters to produce the free developers and the boronic acid side product. Usually the pH of the alkaline solutions, used for activation, may be varied to suit particular needs. In preferred embodiments, an alkaline solution having a pH in excess of 9 is employed.

The cyclic esters for use in this invention may be prepared by a simple condensation reaction between the boronic acid and the α,β-enediol developer.

The following nonlimiting example illustrates the preparation of a cyclic developer within the scope of the present invention.

Example 1

10 g. of catechol was dissolved in 20 cc. of hot water and added with stirring to 10 g. of phenylboronic acid which was dissolved in 150 cc. of hot water. The product crystallized out on cooling.

The following nonlimiting example illustrates the preparation and use of a photosensitive element within the scope of this invention.

Example 2

A coating solution was prepared by mixing together the following: 26 cc. of a stabilized iodobromide silver halide emulsion, 4.00 cc. of a 12.5% solution of catechol benzene boronate in methanol, 2.00 cc. of a 10% saponin solution in water, a wetting agent and 0.8 cc. of a 10% acetic acid solution. The resulting coating solution was applied to a suitable support.

The photosensitive element prepared in Example 2 was tested in a diffusion transfer process. In this test the emulsion was exposed and wet with a processing solution comprising:

Water, cc.	200
Sodium hydroxide, g.	10.34
Sodium carboxymethylcellulose, g.	8.06
Sodium thiosulfate, g.	2.0

and superposed on an image-receiving sheet containing silver precipitating agents. In about 1 minute a sharp clear diffusion transfer image was obtained.

It should be understood that, when desired, the cyclic esters may be placed in layers in the photosensitive elements other than the silver halide emulsion layers. Thus, for example, the esters may be incorporated in reagent layers, barrier layers, separation layers, etc. In such embodiments, the cyclic structure will prevent premature fogging if the developers should migrate into the silver halide emulsion layer.

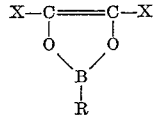
The photosensitive elements of the present invention may be used, for example, in conventional photographic processes; in the preparation of relief images; in gelatin transfer processes; in silver-complex diffusion transfer processes, color processes, color diffusion transfer processes, etc.

Since certain changes may be made in the above product without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

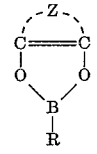
What is claimed is:

1. A silver halide emulsion comprising a cyclic ester of a boronic acid and an α,β-enediol silver halide developing agent.

2. A silver halide emulsion comprising a compound selected from the group represented by the formulae:



and

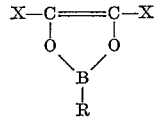


wherein R is an organic radical, each X is a hydrogen or alkyl radical and Z represents the atoms which complete a heterocyclic or aromatic ring.

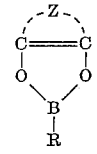
3. A silver halide emulsion comprising a cyclic ester of catechol with phenyl boronic acid.

4. A photographic product comprising a plurality of layers including a silver halide emulsion layer, at least one of said layers having disposed therein a cyclic ester of a boronic acid and an α,β-enediol silver halide developing agent.

5. A photographic product comprising a plurality of layers including a silver halide emulsion layer, at least one of said layers having disposed therein a compound selected from the group represented by the formulae:



and



wherein R is an organic radical, each X is a hydrogen or alkyl radical and Z represents the atoms which complete a heterocyclic or aromatic ring.

6. A product as defined in claim **5** wherein said compound is a cyclic ester of catechol with phenyl boronic acid.

References Cited by the Examiner

FOREIGN PATENTS

559,465	8/1957	Belgium.
812,673	4/1959	Great Britain.

OTHER REFERENCES

J. Org. Chemistry, 19, 780–783 (1954).

NORMAN G. TORCHIN, *Primary Examiner.*

G. H. Bjorge, *Assistant Examiner.*