United States Patent Office

3,420,667

Patented Jan. 7, 1969

3,420,667

SUBSTITUTED QUINONES AND DIIMINE QUINONES AS SILVER HALIDE SENSITIZERS

Ralph A. Copeland, 912 River Road, M.R. 97, Binghamton, N.Y. 13901

No Drawing. Filed Dec. 29, 1965, Ser. No. 517,478
U.S. Cl. 96—107 7 Claims
Int. Cl. G03c 1/28, 1/34

This invention relates to photography, photographic silver halide emulsions and, more particularly, to the manufacture of emulsions having increased speed making them particularly suitable for half-tone and line reproduction purposes.

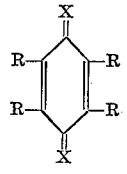
The photographic emulsions which are used for pictorial purposes by professional and amateur photographers are designed to produce upon development a medium or low-contrast image, whereas emulsions used for half-tone and line reproduction in the photomechanical and lithographic field must possess an extremely contrasting image so as to satisfy the critical standards of the lithographer and photoengraver.

The gradation of an emulsion and the film of which it is a part is customarily defined by a graphic analysis of the response to light shown by the film under definite and accurately controlled conditions of exposure and development. For this purpose, the film is exposed in a sensitometer and developed under controlled and standardized conditions. The resulting densities are measured and plotted on a graph against the exposure values which produce them. The line drawn through the resulting points is termed the characteristic curve or the H & D curve for the particular sample. Inasmuch as most photomechanical processes require a film of extremely high contrast, optimum results are obtained only when all of the highly exposed portions of the negative have the same high density and when the unexposed or underexposed portions of the film are completely clear. Thus, the characteristic curve of an ideal graphic arts film would portray an abrupt exposure differential between the minimum and maximum density regions. The attainment of such ideal sensitometric characteristics are not presently possible, and the characteristic curves of films for half-tone and line copy purposes always possess a somewhat extended intermediate exposure range. In an attempt to decrease the intermediate exposure range, the art has resorted to a wide variety of additives which, although accomplishing the desired purpose of improving the intermediate exposure range, nevertheless reduced the speed of the resulting photographic emulsions.

It is, therefore, the primary object of this invention to provide a novel process for increasing the speed of a photographic emulsion.

It is a further object of this invention to provide a novel process for increasing the speed of photographic emulsions particularly adapted to be employed for half-tone and line reproduction purposes.

It has now been found that the above objects can be obtained by incorporating into a gelatin-silver halide emulsion a quinone or imine compound corresponding to the following formula:



wherein X is selected from the group consisting of oxygen and the radical Ny wherein y is selected from the group consisting of hydrogen and alkyl radicals of from 1 to 10 carbon atoms and each of R is individually selected from the group consisting of hydrogen, halogen and alkyl radicals of from 1 to 15 carbon atoms.

Specific compounds falling within the above formula would include benzoquinone, tetrachlorobenzoquinone, tetrabromobenzoquinone, tetraethylbenzoquinone, tetramethylbenzoquinone, p-quinone diimine, p-quinone imine, 2,5-dimethylbenzoquinone, 2,5-diethylbenzoquinone, 2,6-dichlorobenzoquinone, etc.

The gelatin silver halide emulsions used in the instant invention are unsensitized, orthochromatic or panchromatic, high-contrast emulsions. These emulsions are developed with the socalled infectious type developers which contain, in addition to a developing agent of the hydroquinone type, a mixture of paraformaldehyde and potassium metabisulfite or the reaction product of a formaldehyde and sodium bisulfite as described in U.S. Patent 2,313,523. The infectious developers normally produce images possessing gamma values of approximately 8.0.

The lithographic developers which are used in the infectious type of developers differ from the conventional developers by containing only a small and controlled amount of free sulfite ions. The major amount of the alkali sulfite which is contained in the developer solution is kept in reserve in the form of a formaldehyde-bisulfite addition compound which acts as a sulfite buffer. If too much sulfite is present, infectious development will not occur, and if too little is available, a high fog level will result.

The developers differ also from conventional developers to the extent that the development time is somewhat critical if images of maximum gamma are desired. Development times which are shorter or longer than the optimum durations will yield low gamma values. The highest gamma values are obtained within a development time ranging from 1½ minutes to 4½ minutes.

The silver halide used in the preparation of these emulsions is silver chloride, silver chlorobromide or silver bromide.

Small concentrations of iodide can be tolerated if the silver iodide content of the emulsion does not exceed 3.0 mole percent based on the amount of silver nitrate used in the preparation of the silver halide emulsions. When silver chlorobromide emulsions are used, the relative amount of halides generally ranges from 2 to 8 parts of chloride per part of bromide.

The amount of quinone or imine compound which is employed in the novel process of this invention ranges from 0.1 to 1.0 grams per kilogram of liquid silver halide emulsion; the preferred range is between 0.3 and 0.6 gram per kilogram of silver halide emulsion.

In practicing the present invention the quinone or imine compound is dissolved in a suitable solvent, preferably a low boiling alcohol such as methanol, ethanol, propanol or isopropanol and thereafter added to the silver halide emulsion either during the ripening stage or just prior to coating the desired film base.

It is well known that emulsions of the types which are to be used in the graphic arts industry must be highly hardened to withstand the drastic conditions employed in their processing. Formaldehyde, glyoxal, mucochloric acid, mucobromic acid and other organic hardening agents of the type known in the photographic art have been found suitable and can be employed in the instant

invention. In this type of hardening an excess of hardener is used in combination with phenol, resorcinol or resorcinol aldehydes as described in U.S. Patent 2,553,506.

The following examples serve to illustrate the invention but it is to be understood that this invention is not to be restricted thereto.

EXAMPLE 1

High contrast lithographic emulsion formula

Part I:		
Water	liters	5.0
Potassium bromide	grams	7.0
Sodium chloride	do	15.5
Gelatin	do	350.0
Part II:		
Water	liters	1.0
Potassium bromide	grams	63.0
Sodium chloride	do	140.0
Part III:		
Water	liters	1.0
Silver nitrate	grams	500.0

At a temperature of 70° C., parts II and III are added simultaneously over a period of one to two minutes. After the addition is completed, 175 grams of dry gelatin is added and the whole mixture is digested for 30 minutes. The emulsion is chilled, shredded and washed in running water to conductivity of 2000 to 2500×10^6 ohms^{-1}. The emulsion is reliquefied at 40° C. and is then ripened at 55° for 1 hour to permit the attainment of optimum sensitivity. The above emulsion contains 80 mole percent of silver chloride and 20 mole percent of silver bromide.

Prior to coating 30 milliliters of a 1% by weight solution of benzoquinone in methanol was added to 10 kilograms of the above emulsion along with the following:

	Milliliters
Sodium benzene sulfinate (20%)	50
Saponin (5%)	140
Formaldehyde (5%)	20
Resorcinol (10%)	400
Orthochromatic sensitizing dye (1:2000)	900

The emulsion batches are then coated onto cellulose acetate film base and after exposure in a type 11B sensitometer, the exposed films are developed for 3 minutes in the following lithographic developer which is described in the "Ansco Graphic Arts Handbook," p. 38 (1958):

Water	ccs	2,000.0
Sodium sulfite, anhydrous	grams	120.0
Paraformaldehyde	do	30.0
Potassium metabisulfite	do	10.5
Boric acid (crystals)	do	30.0
Hydroquinone	do	90.0
Potassium bromide	do	6.0

Water to make 4.0 liters.

The solution is allowed to remain for 2 hours in a stoppered container before use to permit the formation of formaldehyde bisulfite. The speed of the emulsion is measured and found to be 50% faster than an emulsion process in identically the same manner with the exception that no benzoquinone is added.

EXAMPLE 2

The process of Example 1 was repeated with the exception that 60 milliliters of a 1% methanol solution of benzoquinone was added. The speed of the resulting emulsion was shown to have a 100% increase over the untreated standard.

EXAMPLE 3

The procedure of Example 1 was repeated with the exception that 120 milliliters of a 1% methanol solution of benzoquinone was added. The speed of the resulting emulsion was found to have a 150% increase over the untreated standard.

EXAMPLE 4

The procedure of Example 1 was repeated with the exception that 30 milliliters of a saturated solution prepared by adding 2 grams of tetrachlorobenzoquinone to 200 milliliters of methanol was employed. When compared against the untreated standard this emulsion showed an increase in speed of 100%.

EXAMPLE 5

The procedure of Example 4 was repeated with the exception that 60 milliliters of solution were employed. This resulted in an emulsion having a speed of 150% over the standard.

EXAMPLE 6

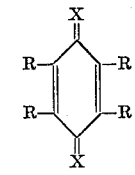
The procedure of Example 4 was repeated with the exception that 120 milliliters of methanol solution were employed. This resulted in an emulsion having a speed substantially the same as that of Example 5.

While the present invention has been described with reference to certain preferred procedures, it is evident that the invention is not to be limited thereto, since many variations may be made to the procedures described therein and that equivalent materials may be substituted without departing from the scope of the invention. For instance, silver chloride and silver chlorobromoiodide emulsions can be used in place of the silver chlorobromide emulsions illustrated in the examples. Synthetic colloidal carrying materials such as polyvinylalcohol or partially hydrolyzed polyvinylacetate can be used in place of gelatin. In place of saponin, synthetic surfactants or wetting agents such as isopropylnaphthalene sulfonic acid or other cationic or non-ionic wetting agents can be used which aid in the preparation of even coatings without bubble formation, provided they do not have any deleterious effect on the photographic preparation properties of the emulsions.

It will be understood, however, that it is not intended that this invention be limited except as necessitated by the appended claims.

What is claimed is:

1. A photographic film comprising a base and a light sensitive silver halide emulsion of the type suitable for halftone reproduction, said silver halide being selected from the group consisting of silver chloride, silver chlorobromide, silver chlorobromoiodide, said emulsion containing from 0.01 to 0.1 gram per 100 grams of silver halide present in the preparation of the emulsion of a compound corresponding to the formula:



wherein X is selected from the group consisting of oxygen and the radical Ny wherein y represents a member selected from the group consisting of hydrogen and alkyl groups of from 1 to 12 carbon atoms and each of R is individually selected from the group consisting of hydrogen, halogen and alkyl groups of from 1 to 12 carbon atoms.

2. The composition of claim 1 wherein the compound is benzoquinone.

3. The composition of claim 1 wherein the compound is tetrachlorobenzoquinone.

4. The composition of claim 1 wherein the compound is p-quinonediimine.

5. The composition of claim 1 wherein the compound is p-quinone imine.

6. The composition of claim 1 wherein the compound is 2,6-dimethylbenzoquinone.

7. The composition of claim 1 wherein the compound is 2,5-dimethylbenzoquinone.

References Cited

FOREIGN PATENTS

645,794 3/1964 Belgium.

NORMAN G. TORCHIN, *Primary Examiner.*

J. R. EVERETT, *Assistant Examiner.*

U.S. Cl. X.R.

96—109