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Mimura et al.

[11] **3,887,333**

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[54] **LIQUID SENSITOMETRY PROCESS FOR PHOTOGRAPHIC EMULSIONS**

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[21] Appl. No.: **414,498**

Related U.S. Application Data

[63] Continuation of Ser. No. 188,059, Oct. 12, 1971, abandoned.

[30] **Foreign Application Priority Data**

Oct. 9, 1970 Japan 45-89103

[52] **U.S. Cl.** ..... **23/230 R;** 23/230 A; 96/27 E; 96/50 R; 96/63; 96/94 R; 356/51; 356/204

[51] **Int. Cl.**...**G01m 21/20;** G01m 33/00; G03c 5/26

[58] **Field of Search** ..... 23/230 R, 230 A, 253 R; 96/27 E, 50 R, 63

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

A process for measuring the photographic properties of an emulsion such as a silver halide by comparing the properties of a first sample of the emulsion that has been exposed to a set quantity of light to a second sample that has not been exposed. Both samples are stirred to insure a uniform mixture and a developer is added to both samples. At the same time, light absorption of both samples is recorded with the help of a pair of fiber optic tubes which are submerged respectively in both samples. The fiber optic tubes transmit light which is non-reactive to the emulsion such as light near the infrared spectrum. The resultant values can be plotted to determine the photographic values.

5 Claims, 6 Drawing Figures

FIG. 1

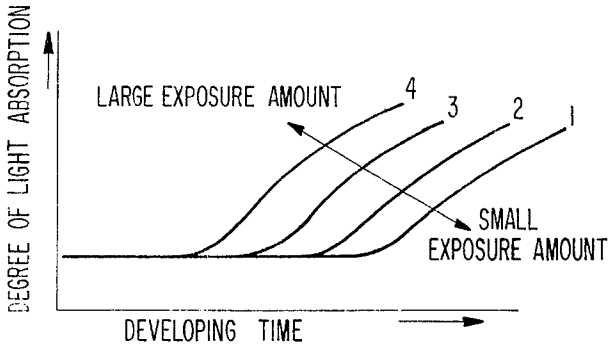
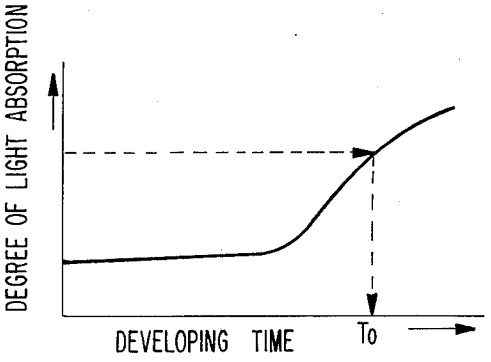


FIG. 2a



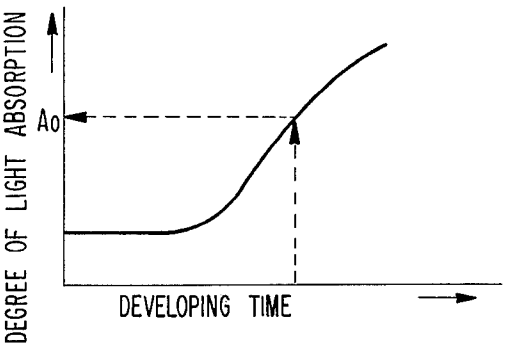


FIG. 2b

FIG. 3

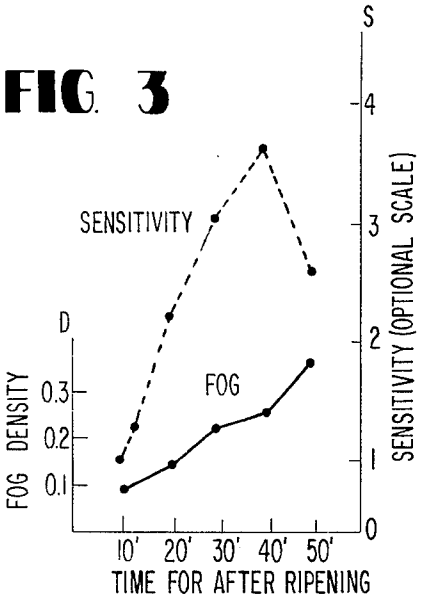


FIG. 4

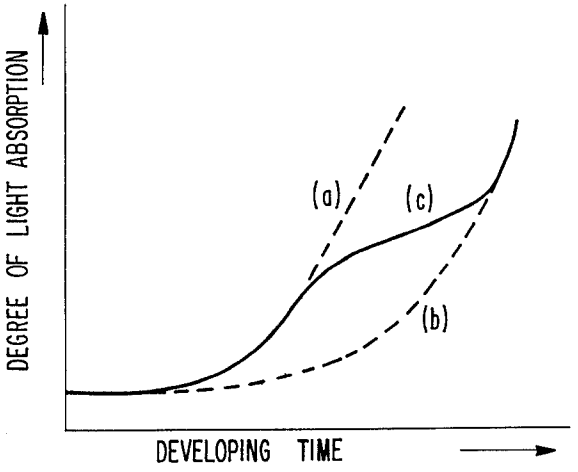
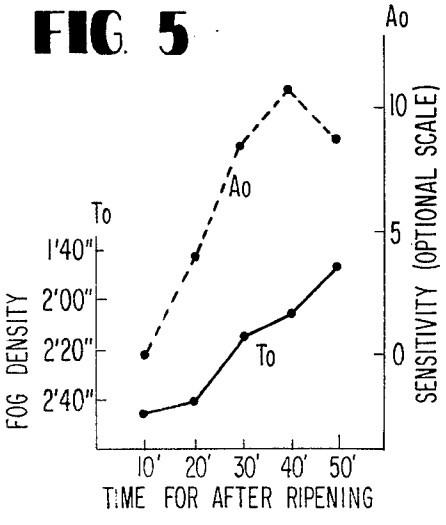


FIG. 5



LIQUID SENSITOMETRY PROCESS FOR PHOTOGRAPHIC EMULSIONS

This is a Continuation, of application Ser. No. 188,059, filed Oct. 12, 1971, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a liquid sensitometry process of photographic emulsions.

2. Description of the Prior Art

Photographic properties of photographic silver halide emulsion, such as sensitivity or fog, have generally been determined by a process in which a gelatino silver halide emulsion is applied to a support and then dried to provide a test piece. The test piece is, after exposure, development and fixing, subjected to a reading of its optical density by means of a densitometer.

The process using such a test piece, however, has problems preventing advancement of the technique of the manufacture of photographic emulsions because the series of coating and drying the photographic emulsion, exposing, developing and fixing the coated emulsion layer, and measuring its density is complicated and requires a long time and a skilled workman to perform the process.

To solve these problems, there has been proposed a liquid sensitometry process in which a photographic emulsion is, in the liquid state, subjected to exposure, development and measurements of photographic properties, see U.S. Pat. No. 2,590,830.

This process, however, includes the step of arresting the development of a large number of samples at predetermined points in the development process, thereby enormously complicating the procedure.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a rapid and practical liquid sensitometry process for photographic emulsion. Another object of the invention is to provide a liquid sensitometry process for photographic emulsion by evaluating the photographic properties from curves of its developing rate. The above object of the invention can be attained by adding developer solutions to both an exposed portion of a silver halide photographic emulsion and to another portion of the emulsion which has been previously subjected to a predetermined quantity of exposure respectively and then, without any addition thereto of any fixing or stopping solution, exposing the emulsion to a light to which the emulsion is not sensitive while constantly stirring also to continuously read the degree of developing rate and to obtain two curves of developing rate for evaluating the photographic properties by comparison of the two curves.

In the process of the present invention, the procedure is simple and results can be obtained more rapidly than in the prior liquid emulsion sensitometry process because the determination of photographic properties are obtained by reading the degree of developing rate from a mixture of an emulsion with a developer solution without addition of any fixing or stopping solution. In addition, since the photographic properties are determined by the curves, they can be obtained as a pattern having a large amount of information with a good degree of accuracy.

The developing rate is measured by the following procedure:

1 a liquid emulsion and a diluent are incorporated into a vessel and stirred,

2 the mixture is exposed to a required quantity of exposure, if necessary,

3 a developer solution is then added to the mixture while stirring, and

4 while maintaining the stirring, the mixture is exposed to a light to which the emulsion is not sensitive, while measuring continuously the absorption of the emulsion to obtain a curve of the developing rate.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is explanation curves showing a developing ratio obtained in the process of the present invention, in which the curves shift from **1** to **4** corresponding to the amounts of exposure;

FIGS. **2***a* and **2***b* are illustrative graphs for determining photographic properties using the curves of developing rate obtained in the process of the present invention;

FIG. **3** is an illustrative graph for determining the photographic properties using a conventional sensitometry process;

FIG. **4** are the curves showing developing rates of emulsion exposed to different conditions of exposure, and

FIG. **5** is an illustrative graph similar to FIG. **3**.

DESCRIPTION OF THE PREFERRED EMBODIMENT

A photographic silver halide emulsion and a diluent are put in a vessel and stirred into a homogeneous mixture. The silver halide emulsion may be any of those having usually been used in light-sensitive photographic materials. For example, a silver halide such as silver chloride, silver bromide, silver iodide, silver chlorobromide, silver iodobromide, silver chloroiodobromide, etc., is dispersed in an aqueous solution of a natural high molecular substance such as gelatin, or synthetic high molecular substance such as polyvinyl alcohol or mixture thereof. The diluent may be exemplified by water and aqueous solution of gelatin, and the amount thereof is not limited so long as the emulsion can be uniformly dispersed therein and be blackened to give density suitable for measurement when exposed and developed.

The stirring of the mixture is not significant, but it is necessary to provide a uniformly diluted solution. The emulsion thus diluted is exposed under conditions of quantity of light and length of time appropriate for the emulsion.

To the emulsion thus exposed is then added a developer solution while stirring. There should be used a developer solution suitable for the emulsion to be tested, such as, hydroquinones, 3-pyrazolidones, p-aminophenols or mixtures thereof. The emulsion is then exposed to light to which the emulsion is not sensitive, with the progress of development to measure the light absorption. In this case, the value of light absorption may be measured for instance, by imposing a pair of optical fibers in the vessel containing the mixture of emulsion and developer solution, the optical fibers being so aligned that one end of an optical fiber is opposite at a distance to one end of the other optical fiber in the vessel, applying a light such as an infrared ray

from one of the optical fibers and measuring the transmitted light in the other one of the optical fibers to read the light absorption value. Thus, the densities of the developed silver halide are continuously measured and recorded in terms of light absorption value versus developing rate so that the data required for determination of the photographic properties of the emulsion can be obtained within a few minutes.

The advantages according to the present invention are as follows:

1 Since the process of the present invention makes it possible to rapidly and definitely determine the end point of ripening in the manufacture of emulsions, there are obtained emulsions of uniform and improved qualities, and

2 since it is possible to read whole photographic properties at once, the number of workers can be reduced and the storage amount of emulsion which is used in manufacturing a light-sensitive photographic materials from the result of the test can be remarkably decreased.

A curve of developing rate of an unexposed emulsion is determined by the present process of the invention and a developing time corresponding to a prefixed value of light absorption in the curve is set as a characteristic value T_o as shown in FIG. 2*a*. On the other hand, a curve of an emulsion which has been previously exposed to a prefixed amount of exposure is determined by the process of the invention and a value of light absorption at a prefixed developing time in the curve is set as a characteristic value A_o as shown in FIG. 2*b*.

T_o and A_o are determined for several parts of an emulsion sample which is, after being ripened or reacted for different periods of time, plotted on a graph to obtain curves, as shown in FIG. **5**, corresponding to the results of a prior sensitometry process developing time for 4 minutes using an emulsion applied to a glass plate of film as shown in FIG. **3**.

The FIG. **5** indicates that, in the process of the present invention, there are obtained similar results as in the prior processes, and that the liquid sensitometry process is applicable to control the advance of after-ripening in the manufacture of emulsions having a high sensitivity and a low fog.

For example, in the case of producing a photographic emulsion of which fog at a maximum sensitivity is prefixed, the fog increase rate of the emulsion to time are measured during the initiation period of the after-ripening step by the process of the invention to obtain some results which are then plotted to form a curve, from which the time of after-ripening cocorresponding to the prefixed value of fog is obtained. Thus, the afete ripening of the emulsion in practical scale is determined at the time. The sensitivity can be measured by substituting sensitvity for fog in the above description.

By this process, stable photographic emulsions can be produced from any suitable raw materials in any conditions.

In FIG. **4**, when the emulsion is uniformly exposed, the curve (a) formed by the measurement is obtained; when the emulsion is unexposed, the curve (b) is obtained; and when the emulsion is partially exposed, the curve (c) is obtained. Accordingly, since the curve (c) is obtained if problems such as fog are caused in the production of emulsion, they can be easily found by checking the curve obtained by the process of the invention.

The present invention is illustrated in more detail by the following example.

EXAMPLE

To a vessel were added 5 cc of a test specimen of a gelatino silver iodobromide emulsion and 500 cc of an aqueous inactive gelatin solution as diluent and the mixture was subjected to an exposure of 0.1 CMS. In the vessel, there were then imposed optical fibers and 500 cc of a phenydone-hydroquinone developer solution was added to develop the emulsion at 20° C to 40° C.

During the progression of the development, the value of light absorption was continuously measured on the emulsion in the vessel by the aid of a near infrared ray (wavelength 0.9 μ) to obtain a curve as shown in the FIG. 2*b*.

On the other hand, the same emulsion as above was processed in the same manner without exposure to obtain a curve as shown in FIG. 2*a*.

The time required to obtain the final data which indicated the photographic properties of the emulsion was only 3 minutes.

While the above is the preferred form of the inventive process it is clear that variations are possible to one skilled in the art and accordingly, the scope of the invention should be measured only from the following claims.

What is claimed is:

1. A process of continuously determining the photographic characteristics of a photographic silver halide emulsion, which process comprises the steps of:

a adding a developing solution to a first sample of a photographic emulsion which has not been exposed to light and to a second sample of the photographic emulsion which has been exposed to a predetermined quantity of light;

b continuously measuring the development rate during the development of each of said samples by using light having a wavelength to which the photographic emulsion is not sensitive and measuring the amount of said light absorbed by each of said samples; and

c comparing the resultant measurements for each of said samples to determine the photographic properties of the photographic emulsion.

2. The process of claim **1**, including the further step of continuously stirring each of said first and second samples to ensure uniform samples.

3. The process of claim **1** wherein the wavelength of the light used to continuously measure the development rate of the emulsion during the development of each of said samples has a wavelength in the infrared spectrum.

4. The process of claim **3**, including the further step of continuously stirring each of said first and second samples to ensure uniform samples and wherein the light used to continuously measure the development rate of the emulsion during the development of each of said samples is transmitted by a pair of optical fibers in each sample.

5. The process of claim **1**, including the further step of continuously stirring each of said first and second samples to ensure uniform samples and wherein the light used to continuously measure the development rate of the emulsion during the development of each of said samples is transmitted by a pair of optical fibres in each sample.

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