April 3, 1973 D. C. SEELBINDER ET AL 3,725,071

METHOD AND APPARATUS FOR CONTROLLING CHARACTERISTICS OF FOGGED SILVER HALIDE EMULSIONS

Original Filed Oct. 30, 1968

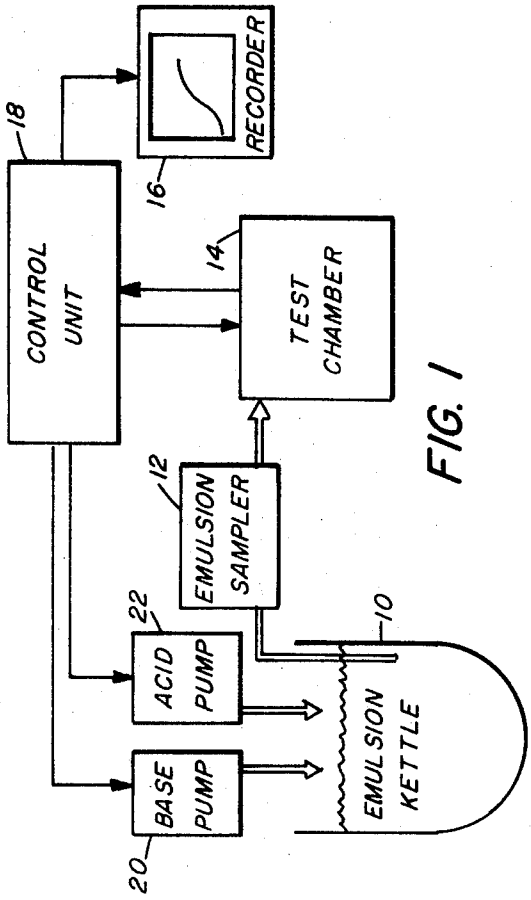


FIG. 1

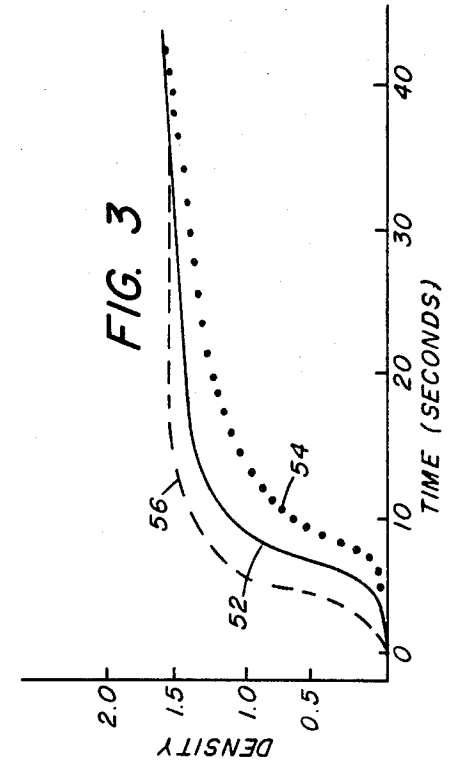


FIG. 3

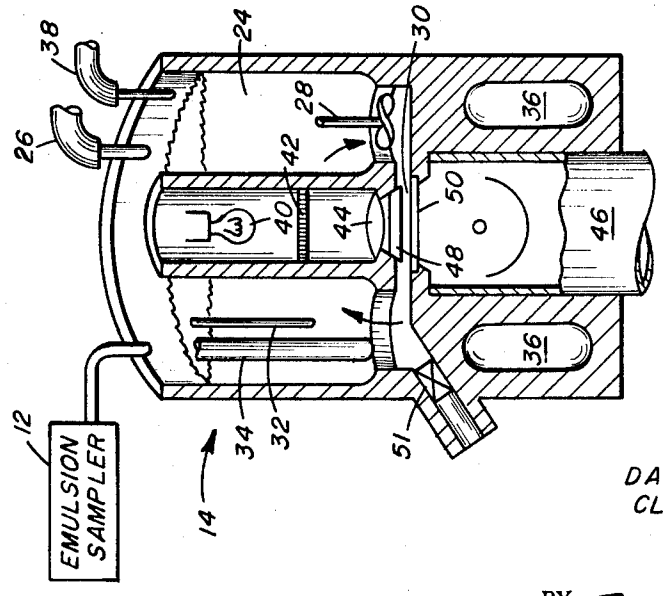


FIG. 2

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United States Patent Office 3,725,071
Patented Apr. 3, 1973

3,725,071

METHOD AND APPARATUS FOR CONTROLLING CHARACTERISTICS OF FOGGED SILVER HALIDE EMULSIONS

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Continuation of abandoned application Ser. No. 771,925, Oct. 30, 1968. This application Mar. 29, 1971, Ser. No. 129,259

Int. Cl. G03c 1/02

U.S. Cl. 96—94 8 Claims

ABSTRACT OF THE DISCLOSURE

Method and apparatus for maintaining optimum fog levels in fogged silver halide emulsions by controlling the development rate characteristics thereof. A developing agent is added to a sample of the liquid emulsion prior to its coating on a substrate, and the density of the developing sample is measured at first and second time intervals following the addition of the developer. The ratio of the two density measurements is then compared with a predetermined value representing optimum development rate characteristics, and the pH of the emulsion is altered in the event the measured density ratio differs from the predetermined value, the pH being increased in the event the density ratio is less than the predetermined value, and decreased if the density ratio is greater than the predetermined value. The pH of the emulsion is held at this higher or lower value for such time as is required to bring the density ratio of the emulsion to approximately the predetermined value representative of optimum fog level just prior to coating.

This application is a continuation of application Ser. No. 771,925 filed Oct. 30, 1968, now abandoned.

This invention relates to photographic emulsions and, particularly, to the control of fog level in fogged silver halide emulsions.

Fogged silver halide emulsions (i.e., emulsions which have already been exposed to light or to its chemical equivalent) are used in direct positive photographic films and papers, as well as in direct positive plates for lithographic printing. There are many varieties of direct positive emulsions: for instance, direct positive emulsions based on Herschel Reversal are described in Kendall and Hill U.S. Pat. 2,541,472 and British Pat. 723,019; direct positive emulsions containing silver halide crystals having internal electron traps are described in Berriman U.S. Pat. 3,367,778; direct positive solarizing emulsions containing electron-accepting organic compounds are described in Belgian Pat. 695,366.

Although it might seem that fog level could vary quite widely without affecting the intended purpose of this type of emulsion, such is not the case. It has been found that when the fog level of such silver halide emulsions is too low, the maximum density (D-max.) obtainable upon development is insufficient to provide good contrast in direct positive prints and transparencies. On the other hand, if the fog level of the emulsion is too great, the emulsion tends to be less sensitive for use in such direct positive materials. Similarly, when such prefogged silver halide emulsions are used in preparing lithographic printing plate materials such as those disclosed in U.S. Pat. 3,146,104, issued on Aug. 25, 1964 to E. C. Yackel et al., high fog levels in the emulsion result in plates which are quite susceptible to scumming or toning (undesired inking in white areas), and particularly low fog levels can result in insufficient inking in the image areas of the plate material.

Therefore, as can be readily appreciated, it is desirable that the fog level of such emulsions be maintained within predetermined optimum limits in order to assure good quality in the products in which they are used. However, silver halide emulsions for this type of photographic product are usually prefogged chemically during manufacture and then held in cold storage for various periods of time prior to being coated on an appropriate substrate. The fog level of prefogged emulsion often changes during such storage, creating serious quality control problems for the final photographic product.

It is known in the art that the density of a developed silver emulsion coated on an appropriate substrate is roughly proportional to the diffuse infrared density of the same emulsion developed in a liquid state. While this proportionality has definite limitations insofar as it might be used for analytical test purposes to determine precise physical measurements, persons skilled in the art have utilized this rough proportionality to make empirical determinations of exposure characteristics of silver halide emulsions prior to coating. Such prior art determinations have been made by removing samples from the liquid emulsion batch to be tested, exposing the samples to respective graduated amounts of light, developing the samples, and then plotting their respective densities on a continuous recorder to produce an approximate sensitometric exposure curve for that particular emulsion batch. Operating personnel then compare the measured curve with an optimum exposure curve, interpreting any undesirable deviations between the two and making adjustments, accordingly, to the tested batch of emulsion. However, this type of sensitometric testing of liquid emulsions does not help solve the problem of fog level control in prefogged emulsions, since the latter have already been effectively exposed and, therefore, they cannot be tested sensitometrically in the same way as unfogged emulsions.

It is an obejct of the invention herein to measure the fog level of a chemically fogged silver halide emulsion while the emulsion is still in the liquid state, to determine whether or not the fog level departs from a predetermined optimum level, and to adjust the fog level of the emulsion to such optimum level just prior to the time it is coated on a substrate.

It is a further object to make such measurements, determinations, and adujstments in a relatively simple, inexpensive and rapid manner.

The objects set forth above are achieved by the method and apparatus disclosed herein which are based upon the finding that the fog level of a liquid prefogged silver halide emulsion varies in accordance with the development rate of that emulsion. By comparing this rate of development with the rate of development of a similar emulsion having optimum fog levels, i.e., comparing it with a predetermined optimum development rate, it is possible to determine whether or not the particular emulsion being tested departs from the optimum fog level, in what direction that departure exists, and to what extent. Based upon this determination, the pH of the liquid emulsion is then altered for a period of time sufficient to bring the fog level of the emulsion back to the optimum level prior to coating.

According to the invention disclosed herein, it is possible for relatively inexpert personnel to make such development rate determinations and to alter the pH of a particular batch of emulsion to control its fog level just prior to coating. Development rate characteristics are determined by monitoring the density of a developing sample of emulsion at two predetermined intervals after a developing agent is added to the sample. The ratio of these measured densities, which ratio represents the

development rate characteristics of the sample, is then compared to a predetermined value representing the ratio of similar densities found with an emulsion having optimum fog level (i.e., optimum development rate characteristics). The pH of the emulsion being tested is raised or lowered according to the amount that the measured density ratio falls below, or above, the predetermined optimum value. After allowing sufficient time for the density ratio of the emulsion to reach the optimum value, pH is returned to normal levels, and the emulsion is ready for coating.

Other objects, advantages and characteristic features of the subject invention will now be described in detail with reference being made to the accompanying drawings wherein like reference characters designate corresponding parts, and in which:

FIG. 1 is a schematic block diagram of apparatus for carrying out the method disclosed herein;

FIG. 2 is a schematic cross section of a test chamber for measuring the rate of development of the emulsion samples; and

FIG. 3 is a graph showing typical development rate curves for samples being tested in the chamber illustrated in FIG. 2.

Referring first to FIG. 1, emulsion kettle **10** represents a holding vessel of the type known in the art wherein an emulsion is maintained in liquid form prior to its delivery to a coating machine. In order to determine the fog level of the emulsion, an emulsion sampler **12** removes a small portion of the emulsion from kettle **10** and delivers it to a test chamber **14** where it is diluted with distilled water. Next, an appropriate developing agent is added to the test chamber and the rate of development of the fogged silver halide emulsion is measured graphically by recorder **16**. A determination is then made, e.g., electronically by a control unit **18**, comparing the development rate of the emulsion sample with a predetermined optimum development rate in a manner which will be described in greater detail below. In the event that the determination indicates that the fog level of the emulsion in the kettle is below the optimum level, the pH of the emulsion will be increased by the addition of a basic solution to the emulsion kettle by means of pump **20** and, after a period of time sufficient to allow the fog level of the emulsion to reach the desired predetermined level, acid is then added by pump **22** to bring the pH of the emulsion back to approximate neutrality. Similarly, in the event that the measured development rate of the test sample indicates that the fog level of the emulsion in the kettle is greater than desired, the pH of the emulsion is first lowered for a period of time by the addition of acid through pump **22**, followed thereafter by a return to neutrality by the addition of an appropriate amount of base from pump **20**.

Reference will now be made to the sequential operation by control unit **18** of test chamber **14** which is illustrated in greater detail in FIG. 2. Prior to the addition of a small amount of emulsion through emulsion sampler **12**, mixing chamber **24** is filled with a metered amount of distilled water through diluent hose **26**. After addition of the sample, the diluted emulsion is constantly mixed by pump **28** which moves the liquid from chamber **24**, through a narrow passage **30** and back to the chamber as indicated by the arrows. The diluted emulsion is maintained at a constant temperature by means of a temperature sensing probe **32**, heater element **34**, and a cold water cooling jacket **36**.

Next, a metered amount of an appropriate developing agent (of any type well known in the art for reducing developable silver halide to metallic silver) is inserted into mixing chamber **24** through hose **38**. Thereafter, the development rate characteristics of the emulsion sample are monitored by density sensing apparatus comprising a small lamp **40**, an infrared filter **42**, a collimating lens **44**, and an infrared sensitive photomultiplier tube **46**. Two transparent windows **48** and **50** form the walls of narrow passage **30**, being placed approximately .10-inch apart. The output of tube **46** varies with the intensity of the infrared radiation transmitted through passage **30**, said radiation varying in accordance with the density of the developing emulsion being moved through the narrow passage by pump **28**.

With a developing emulsion sample moving through passage **30** in the manner described above, the output of tube **46** gradually decreases as the amount of metallic silver increasingly develops in the sample. As will be appreciated by those skilled in the art, the output of photomultiplier tube **46** is proportional to the transmittance of the emulsion sample, and by inverting this output and amplifying it logarithmically, a signal is obtained which is proportional to the density of the emulsion sample rather than to its transmittance. This density signal is then recorded as a function of elapsed time to provide an indication of the development rate of the emulsion, thereby producing a development rate curve such as those illustrated in FIG. 3.

In actual practice, after the emulsion sample has been added and is fully mixed with the diluent in chamber **24**, and prior to the insertion of the developing agent, the output of photomultiplier tube **46** is adjusted to obtain a zero density output. Recorder **16** is then activated and the measured amount of developer is injected into the mixing chamber, the recorder plotting a continuous trace of density versus time for a period of 45 seconds. Thereafter, the recorder is reset to zero time, and drain valve **51** is opened, discharging the sample solution. Next, drain valve **51** is closed and more water is injected through hose **26**, mixed with residual sample solution remaining in the test chamber, and then drained through valve **51**. This flushing cycle is repeated twice more to purge the chamber of residual sample, and then the mixing chamber is filled once again with fresh distilled water in preparation for the next test sample.

According to the preferred form of the invention herein, it has been found that a reliable indication of development rate can be obtained quite simply by making only two density measurements after developer has been added to the test sample, and in order to provide a more detailed explanation of this preferred embodiment, the following discussion will assume that the disclosed method is being used to control the development rate characteristics of a fogged silver halide emulsion to assure that, just prior to coating, the emulsion will have development rate characteristics such as those represented by solid-line curve **52** in FIG. 3.

It has been found that a reliable indication of development rate can be provided in the form of an appropriate "guide number" determined simply from only two density measurements in the manner indicated by the following mathematical statement:

$$G=\frac{D(t_1)}{D(t_2)}\times 100$$

where G is the guide number, $D(t_1)$ is then density of the test sample at the end of a first time period following the addition of the developing agent, and $D(t_2)$ is the density of the sample at the end of a second time period immediately following the first time period. For purposes of simplicity, the resulting fraction is converted to a whole number by multiplying it by the factor 100. Also, while satisfactory results can be obtained using many different possible combinations of time periods for (t_1) and (t_2), the preferred embodiment employs time periods of 10 seconds and 40 seconds, respectively. Attention is called to the fact that other mathematical methods might be used to obtain an indication of development rate, e.g., including vector analysis and integration of areas under the plotted curve. However, because of its simplicity and

reliability, the above formula is employed in the preferred form of the invention.

Application of the just-described density ratio in the invention herein will now be illustrated by specific examples applying the general formula set forth above to the specific development curves indicated in FIG. 3.

Referring first to curve **52**, representing optimum development rate characteristics for a particular type of prefogged silver halide emulsion (such as that disclosed in Example 3 of U.S. Pat. 3,146,104, referred to above), it can be seen that the density measurement taken after 10 seconds is 1.10 and the density measurement made after 40 seconds is 1.50. Inserting these figures in the above formula, a "guide number" of "73" is obtained. This indicates the "guide number" which should be obtained with a batch of similar prefogged silver halide emulsion if that emulsion is to have optimum fog level just prior to the time it is coated on a substrate.

In the first specific example, a batch of such emulsion is sampled and tested by development in test chamber **14** in the manner described in detail above. It is found that the test rate sample has a rate of development as indicated by the dotted-line curve **54** in FIG. 3, recording a slower-than-optimum development rate with a density of 0.75 at the end of the 10-second interval following development, and a density of 1.50 at a period ending 40 seconds after addition of the developer into the test chamber. Inserting these figures in the formula above, i.e., determining the ratio of the densities measured at these two time periods, a "guide number" of "50" is obtained. Comparing this density ratio with the predetermined value "73," it is determined that the fog level of the emulsion so tested is too low to provide desired quality in the final photographic product. Therefore, the pH of the emulsion is raised from 6.7 (a pH of 6.7 approximates neutrality for this type of emulsion) to 7.5 and is held at that level for approximtely 30 minutes. After this excessively basic period the pH is again lowered to 6.7 and the emulsion tested again. The "guide number" obtained is "75," indicating that the development rate characteristics of the emulsion now approximate the optimum characteristics desired.

For the second example, a second batch of fogged silver halide emulsion, similar to that referred to in the preceding paragraph, is tested in the manner described above preparatory to coating on a suitable substrate and is found to have a faster-than-optimum development rate curve such as that illustrated by the dashed line **56** in FIG. 3. The developing density of the test sample after 10 seconds is 1.35, and after 40 seconds the density is 1.50. The ratio of these density figures provides a "guide number" of "90" indicating a fog level considerably above that represented by the predetermined optimum value "73." In order to bring the fog level of the emulsion down to more acceptable levels, the pH of the emulsion is lowered from pH 6.7 to pH 5.5 and held at this level of acidity for 30 minutes. Therefter the pH of the emulsion is again returned to 6.7 and it is once more tested. The guide number is found to be "72," indicating that the emulsion has returned to a fog level approximating the desired optimum value.

As those skilled in the emulsion-making art will appreciate, the amount of time required to bring a particular emulsion back to optimum fog levels will depend upon the degree to which the batch varies from the norm and upon the mount of acid or base used to lower or raise, respectively, the fog level, the amount of acid permissible varying with the type of emulsion, possibilities of local concentrations within the emulsion, etc.

While the curves in FIG. 3 trace densities continuously throughout the test period, it can be understood from the above examples that for successful practice of the invention herein it is only necessary to test the density of the emulsion sample at the end of two preselected time intervals. It can also be appricated that (a) the density measurements, (b) the determination of the ratio for the first and second density measurements, and (c) the comparison of the determined density ratio with a predetermined optimum value, followed by (d) appropriate raising or lowering of the pH of the emulsion being tested for a time period sufficient to bring the density ratio of the emulsion back to approximately the predetermined optimum value, can all be accomplished in an automatic manner by appropriate circuitry designed for such purposes by those skilled in the art of automation.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A method for establishing the development rate characteristic of a liquid, chemically prefogged, silver halide emulsion, comprising:

periodically removing a liquid test sample from the emulsion;

adding an agent to the liquid test sample for developing the silver halide therein to metallic silver;

measuring the optical density of the developing liquid test sample as a function of time to determine the development rate characteristic of the emulsion;

comparing the development rate characteristic of the emulsion as derived from the test sample with an optimum development rate characteristic for the emulsion;

adding to the emulsion one of a basic solution and of an acid solution for varying the pH of the emulsion to effect a development rate characteristic substantially equivalent to that of the optimum development rate characteristic; and

adding to the emulsion, after the optimum development rate characteristic has been achieved, the other of the basic solution and of the acid solution for adjusting the pH of the emulsion to approximate neutrality.

2. A method for establishing the development rate characteristic of a liquid, chemically prefogged, silver halide emulsion, comprising:

periodically removing a liquid test sample from the emulsion;

adding an agent to the liquid test sample for developing the silver halide therein to metallic silver;

measuring the optical density of the developing liquid test sample at the end of a first time period following the addition of the agent;

measuring the optical density of the developing liquid test sample at the end of a second time period following the first time period;

determining the optical density ratio of the first optical density measurement to the second optical density measurement;

comparing the optical density ratio derived from the liquid test sample with an optimum optical density ratio related to the optimum development rate characteristic for the emulsion;

adding to the emulsion one of a basic solution and of an acid solution for varying the pH of the emulsion to effect a development rate characteristic substantially equivalent to that of the optimum development rate characteristic for the emulsion; and

adding to the emulsion, after the optimum development rate characteristic has been achieved, the other of the basic solution and of the acid solution for adjusting the pH of the emulsion to approximate neutrality.

3. The method according to claim **2**, wherein said liquid test sample is diluted prior to the addition of the developing agent.

4. The method according to claim **2**, wherein said time periods are selected on the basis of the expected develop-

ment rate characteristic of an emulsion having the optimum development rate characteristic, the second time period being sufficient to allow substantially maximum density development of the liquid test sample, and the first time period coinciding with development producing from about 60% to about 85% of the miximum density for the liquid test sample.

5. The method according to claim 4 wherein the optical density measurements comprise sensing the intensity of radiant energy passing through the liquid test sample.

6. The method according to claim 5 wherein the liquid test sample is subjected to radiant energy having wavelengths longer than 740 mμ.

7. A method for establishing the development rate characteristic of a liquid, chemically prefogged, silver halide emulsion, comprising:

periodically removing a liquid test sample from the emulsion;

diluting the liquid test sample in distilled water;

adding a silver developing agent to the diluted liquid test sample;

while mixing the developing, diluted liquid test sample and passing a portion thereof through a narrow passage transparent to infrared radiation, directing infrared radiation onto said passage;

sensing the intensity of the infrared radiation passing through said developing liquid test sample at first and second intervals of time following addition of the developing agent;

determining the inverse ratio of the infrared intensity sensed at the first interval to that sensed at the second interval;

comparing the determined inverse ratio with an optimum ratio related to the optimum development rate characteristic of the emulsion;

adding to the emulsion a basic solution, when the optimum ratio is greater than the inverse ratio, and an acid solution, when the optimum ratio is less than the inverse ratio, for varying the pH of the emulsion to effect an inverse ratio that is approximately equal to said optimum ratio; and

adding one of the basic and acid solutions to the emulsion, after the optimum ratio has been achieved, for adjusting the pH of the emulsion to approximate neutrality.

8. The method according to claim 1 wherein the second adding step comprises adding the basic solution to the emulsion to increase its pH, when the development rate characteristic of the liquid test sample is less than the optimum development rate characteristic, and adding the acid solution to the emulsion to decrease its pH, when the development rate characteristic of the liquid test sample is greater than the optimum development rate characteristic.

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U.S. Cl. X.R.

96—59, 63, 64, 66