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REGENERATION OF PHOTOGRAPHIC DEVELOPER SOLUTIONS

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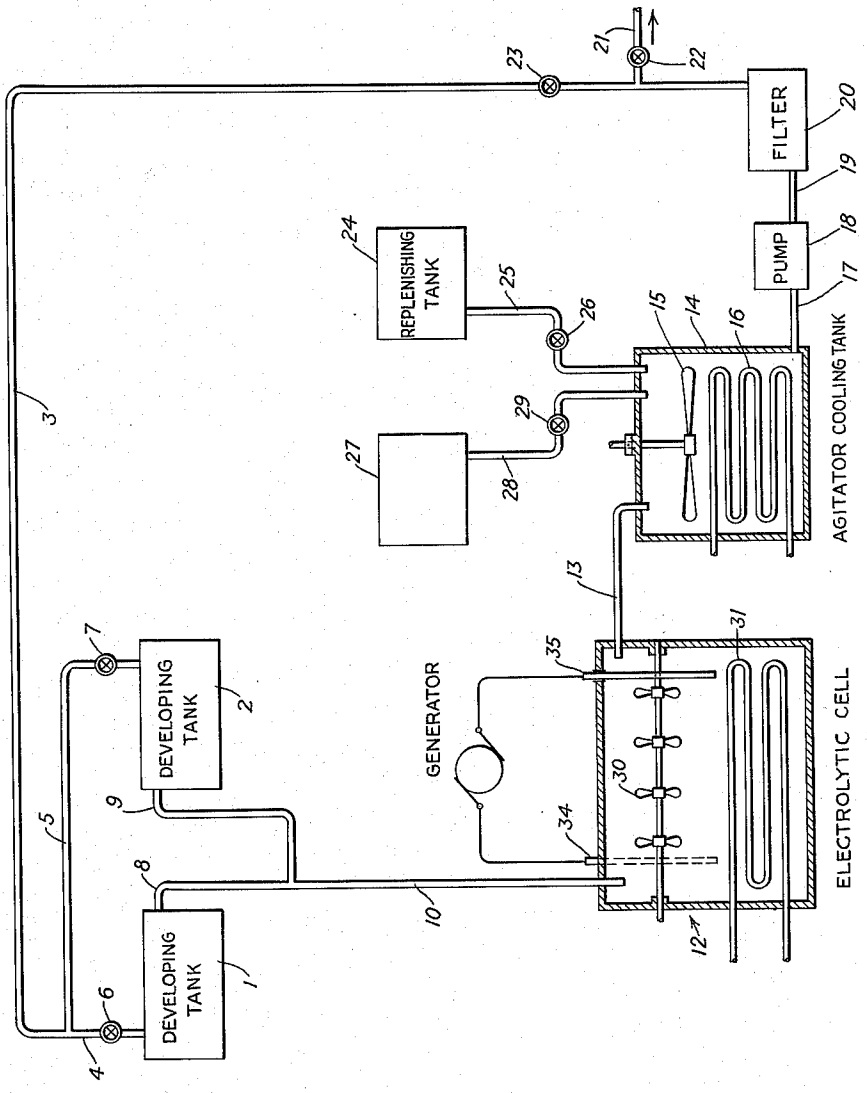

Fig. 1

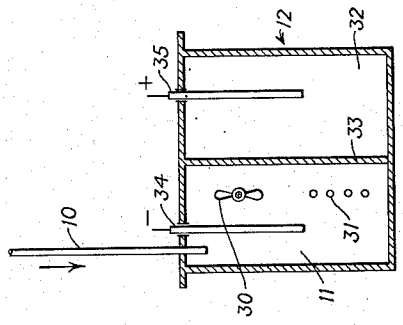

Fig. 2

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REGENERATION OF PHOTOGRAPHIC DEVELOPER SOLUTIONS

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6 Claims. (Cl. 204—9)

This invention relates to new and useful improvements in the regeneration of photographic developer solutions and in systems incorporating such regeneration in combination with continuous recirculation.

The methods employed in the development of the photographic image are well known. The developer solution consists usually of an organic reducing agent, such as hydroquinone or methyl para aminophenol sulphate, in combination with sodium sulphite, sodium carbonate, and potassium bromide. The organic reducing agent is usually referred to as the developer. The function of the reducing agent or developer is to convert that part of the silver halide which has been acted on by light to metallic silver. The sulphite serves to protect the developer solution from oxidation by the air. The carbonate provides the necessary alkalinity. The bromide is added as a "restrainer", and its function is to retard the rate of development so as to produce the desired density and contrast.

With continued use of the developer solution, the concentration of the developer becomes less on account of the oxidation which takes place. Simultaneously there is an equivalent increase in bromide concentration due to liberation of bromide from the silver bromide in the emulsion. The decrease in developer concentration and increase in bromide concentration decrease the rate of development. In usual practice, developer is added to the solution at intervals to compensate for these changes. After the developer solution has been used for some time, it reaches a point where it is no longer economical to continue its use, because increasingly large additions of developer are required to offset the accumulated bromide. By the time this condition is reached, the solution has usually become dark colored and turbid, with a tendency to staining.

One object of this invention is to provide a simple and inexpensive means of regenerating developer solution and reducing the cost of development.

Another object of the invention is to provide means of reducing oxidized developer.

Another object of the invention is to provide means of removing accumulated bromide from the developer solution.

Another objects of the invention is to provide a method of maintaining substantially constant concentrations of developer and bromide in the developer solution so that uniform results are obtained.

Another object of the invention is to provide a method of maintaining substantially uniform developing characteristics in photographic developer solutions.

Another object of the invention is to provide means of maintaining a substantially uniform temperature in the developing solution regardless of external conditions of temperature.

Another object of the invention is to provide means of clarifying the developer solution.

Another object of the invention is to prevent staining which results from the long continued use of developer solutions.

Other objects and advantages of the invention will be apparent as it is better understood by reference to the following specification and to the accompanying drawing, in which

Fig. 1 illustrates diagrammatically an apparatus which may be used in carrying out the invention; and

Fig. 2 is a transverse section through the electrolytic cell.

The invention is particularly applicable to large scale industrial operations such as the development of motion picture film and similar commercial photographic work.

In the practice of the invention, the developer solution is electrolyzed in a cell, which is divided into two compartments by a suitable diaphragm, the developer solution being in the cathode compartment. The anode compartment may contain any suitable electrolyte, such as a solution of sodium hydroxide, sodium carbonate, or sodium sulphate, but we prefer to use a solution which is alkaline. As a diaphragm, we may employ any porous material which prevents mechanical mixing of the solution in the two compartments without preventing the passage of electric current or migration of the bromide ion. Suitable diaphragm materials are unglazed porcelain, clay, asbestos, carbon, carborundum, or graphite. The cathode is preferably a metal of high hydrogen overvoltage, such as lead or zinc, but other metals, gas carbon or graphite may be employed. The anode may be of any metal not attacked by the solution in the anode compartment. In alkaline solution, we prefer to use nickel anodes. The electrolytic cell may be made of any suitable material, for example rubber lined steel. Means of agitating the solution during electrolysis are advisable.

The cathode current density employed varies with the developer used and its concentration, as well as the concentration of other ingredients in

the solution. In practice, the cathode current density will be regulated so as to give as high current efficiency as possible in reduction of developer. The required current density is obtainable with a voltage of approximately 6 to 12 volts. The anode current density is not important and may vary within extremely wide limits. The temperature at which electrolysis is carried out is subject to wide variation, but preferably the temperature is maintained near the most desirable temperature for development (approximately 60–70° F.).

As the electrolysis proceeds the oxidized developer is reduced at the cathode. Bromide, which exists in the solution as bromide ion, travels towards the anode and passes through the diaphragm, out of the developer solution, into the anode compartment. The developer solution becomes lighter in color. Spent developer solution approaches new developer solution in appearance and effectiveness after electrolysis.

While the method is utilized most economically in a system involving circulation of the developer solution, it may be applied as a batch operation as well, that is to say, the spent developer solution may be withdrawn and treated in accordance with this invention. Such an operation may be used advantageously because treatment in accordance with the invention regenerates the solution and renders it fit for reuse.

As an illustration we may describe the result of treating by the present method a batch of developer solution which was almost ready to be thrown away. Before treatment, the developer was very dark and turbid. This turbidity could not be removed by filtration, even with a filter aid. The time required to obtain complete development was three minutes. The solution was electrolyzed at 8 volts for two hours, and then filtered. The filtered solution was about the same color as a new developer solution and perfectly clear. The time required for development with this treated solution was one and one-half minutes. Film developed for this same time in the untreated solution was considerably underdeveloped.

In the practice of our invention, we prefer to regulate the extent of the electrolysis so as to restore to the developer solution its original developing characteristics. These may be measured by any suitable method, such as the well known H and D curve which shows the relationship between exposure (expressed logarithmically) and the densities produced.

In the preferred and more economical operation of the invention, the electrolysis is conducted in a substantially continuous manner, the developer solution being withdrawn continuously from the developer bath or baths, electrolyzed and recirculated so as to maintain the level in the developer bath or baths and likewise to maintain substantially uniform concentrations of developer and bromide in the developer solution. The solution is cooled or heated as required to bring it to the right temperature. This facilitates the operation of development and permits obtaining uniformly good results with economy in the use of developer.

In carrying out the invention in its preferred form, we may utilize the apparatus illustrated in the accompanying drawing. Figure 1 illustrates the layout of the circulation system in which 1 and 2 indicate tanks through which film is drawn continuously for development. The developer solution is fed continuously to the tanks 1 and 2 from the return pipe 3 and the branch pipes 4 and 5 which are controlled by valves 6 and 7.

The developer solution is withdrawn continuously through overflow pipes 8 and 9 and delivered through pipe 10 to the cathode compartment of the electrolytic cell 12. From the electrolytic cell the solution is withdrawn through an overflow pipe 13 and delivered to the reserve tank 14 which is equipped with an agitator 15 and a cooling coil 16. The solution is drawn from the reserve tank through pipe 17 by pump 18 and delivered through pipe 19 to filter 20, from which it is returned through pipe 3 for reuse in the developer baths 1 and 2. A pipe 21, connected to the return line, permits the bleeding of any desired portion of the solution in order to avoid excessive accumulation of undesirable impurities. Valves 22 and 23 permit control of the flow of solution to the bleeder and to the return line.

Additional developer solution to replenish the supply may be maintained in tank 24 and delivered to the reserve tank 14 through a pipe 25 controlled by a valve 26. Additions necessary to maintain the pH of the developer solution may be delivered from tank 27 through pipe 28 controlled by a valve 29 to the reserve tank 14.

The electrolytic cell 12 is equipped with an agitator 30 and a cooling coil 31, a cathode compartment 11, anode compartment 32, diaphragm 33, cathodes 34 and anodes 35.

In the continuous operation of the system as described, the concentrations of developer and bromide can be maintained so as to give any desired speed of development. To maintain a steady, uniform condition it is necessary only that the current passing through the electrolytic cell shall be regulated so as to take care of fluctuations in the amount of film developed and corresponding changes in the rate at which developer solution is kept flowing through the developer baths. The current may be regulated manually, or if preferred, by automatic controlling devices. The developer baths can be maintained at the desired temperature, and bromide can be removed continuously and oxidized developer reduced, without impairing or destroying the value of the solution, which is continuously returned for reuse except when the concentration of impurities rises above a predetermined maximum, at which point a portion of the solution can be removed from the system and a suitable supply of replenishing solution can be added.

It is evident that the invention is applicable to other salts of silver which may be used in photographic emulsions, and the term "bromide" as employed in the claims is intended to cover any ion which is equivalent to or used in place of bromide.

Various changes may be made in the details of construction and arrangement of the apparatus and the procedure without departing from the invention or sacrificing any of its advantages.

We claim:

1. The method of regenerating photographic developer solutions which comprises electrolyzing the solution in the cathode compartment of a diaphragm cell and separating bromine in the anode compartment containing an alkaline solution.

2. The method of regenerating photographic developer solutions which have become oxidized through use which comprises electrolyzing the oxidized solution in the cathode compartment of a diaphragm electrolytic cell with a potential of from about 6 to 12 volts.

3. The method of regenerating photographic developer solutions which have become oxidized through use which comprises electrolyzing the oxidized solution in the cathode compartment of a diaphragm electrolytic cell with a potential of from about 6 to 12 volts, and while the solution is at a temperature of about 60° to 70° F.

4. The method of regenerating photographic developer solutions which comprises circulating the solution in a cycle including a developing tank, electrolyzing a portion of the solution substantially continuously in the cathode compartment of a diaphragm cell having an alkaline electrolyte in the anode compartment, separating bromine in the anode compartment, and returning the electrolyzed solution to the developing tank.

5. The method of maintaining substantially uniform concentrations of developer and bromide in photographic developer solutions which comprises substantially continuously electrolyzing at least a portion of the developer solution in the cathode compartment of a diaphragm electrolytic cell at a rate such that reduction of the solution in said cell takes place substantially as fast as the solution is oxidized as the result of the developing operation.

6. The method of maintaining substantially uniform concentrations of developer and bromide in photographic developer solutions which comprises withdrawing a portion of the developer solution from the zone of development, electrolyzing said withdrawn portion of the developer solution in the cathode compartment of a diaphragm electrolytic cell while development is taking place, and at a rate such that reduction of the solution in said cell takes place substantially as fast as the solution is oxidized as the result of the developing operation, and returning the reduced solution to the zone of development.

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