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BROMIDE RECOVERY FROM SPENT DEVELOPERS

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The invention relates to photographic developers and more particularly to the recovery by electrolysis of soluble bromides from spent developers and the subsequent reduction of the silver bromide thus formed to metallic silver.

In photographic developing processes, soluble bromides accumulate in the developer, as it is continuously employed for the development of photographic negatives, to a point where the developer ceases to function satisfactorily. It has heretofore been usual to discard this developer, thus sustaining the loss of the more or less expensive constituents of the developer.

We have found that the bromides may be recovered from spent developer by subjecting it to electrolysis and this in spite of the fact that sulphite and hydroquinone or other developing agent residues are present in the developer which frequently are thought to impede or at least complicate electrolysis. Our invention is a simple operation and comprises subjecting the spent developer in neutral or acid solution to electrolysis in which a silver element constitutes the anode and silver, carbon or other suitable metal constitutes the cathode. Silver bromide is thus formed upon the surface of the silver anode after which the anode may be removed from the rejuvenated developer and placed in caustic soda or potash solution and subjected to electrolysis with the silver bromide coated silver element constituting the cathode and graphite or a noble metal constituting the anode. By such second electrolysis the bromine is split off from the silver which remains as pure metallic silver upon the element which in the second electrolysis constituted the cathode. This silver element may then be reused as the anode in the primary electrolysis of further spent developers.

It is therefore an object of our invention to provide a process for the rejuvenation of spent developers which process may include the reduction of the silver bromide formed to substantially pure silver. Other objects will appear from a perusal of the following specification.

In its simplest form, the process constituting our invention may be carried out in a non-corrosible container such as glass or stoneware. Into this is placed a quantity of spent developer containing, for instance, sodium sulphite and carbonate, hydroquinone, or other developing agent, soluble bromides and other constitutents, although it will be understood that the particular developer treated is immaterial as photographic developers vary in composition according to the process for which they are employed and our process is directed merely to the recovery of soluble bromides from any of the developers customarily employed in the art. A silver anode of suitable size and a cathode preferably constituted of carbon are placed in the developer a short distance apart and a current density of approximately 4 amperes per square foot is conducted between the anode and cathode through the developer. While 4 amperes is approximately that preferred for an average spent developer, we may employ from one to twelve amperes per square foot, depending upon the progress of the recovery operation, it being understood that as the developer becomes more and more rejuvenated (and the bromine removed) the current density may be decreased somewhat. Although the process will work with some degree of satisfaction with an alkaline developer, we have found it more satisfactory to make the developer neutral or slightly acid, prior to the electrolysis, by passing carbon dioxide through the developer or adding a small amount of an acid, such as sulphuric or acetic. After the electrolysis has continued for a short time it will be found that substantially all of the bromide in the developer has been deposited upon and combined with the silver anode to form silver bromide and the developer substantially rejuvenated. It is preferable to perform this electrolysis at a temperature near the freezing point of water, although considerable variation from this temperature is permissible; the process, in fact, being operable even at room temperature.

Following this rejuvenation the developer may be reused in developing processes by suitably balancing it to bring it back to its original formula; boiling the developer, removes bicarbonate or it may be neutralized with caustic alkali. As the foregoing electrolysis has merely removed bromide ions, at the expense of an equivalent or greater amount of sulphite and developing agent, it will be apparent that more sulphite and developing agent, may be added to restore the developer to its original vigor. The advantage in this is, however, that those constituents necessary to be added are substantially less than would be needed to compound a fresh developer of the same bulk and strength and hence a considerable saving is effected.

While we may employ a sheet of silver as the anode in the foregoing electrolysis, it is preferable to employ a porous composite of wires and inert cage material similar to the elements employed in an Edison battery. The cathode may be a relatively small carbon or metal rod as

indicated above, although this may likewise be in sheet form, or other form desired. Since the cathode is protected electrically from corrosion, its nature is not important.

The foregoing electrolysis need not be completed in one operation in a single recovery cell, although this is the simplest embodiment of the invention. For large commercial installations, it is better to have a series of cells, each conducting its individual and partial electrolysis of the developer, with the completely spent developer entering the No. 1 cell and passing through the various cells down through the last one, the developer being subjected to only a short treatment in each cell. Thus, the current density may be adjusted for greatest efficiency for each cell, it being understood that the current density may be gradually reduced a fraction of an ampere as the developer passes along through the various cells, for instance from five to ten cells in number, although more or less may be employed as found desirable to the skilled operator.

Assuming now that we have a silver anode upon which a quantity of silver bromide has been produced by the combination of the electrolyzed bromine with the silver, this silver bromide can now be reduced to substantially pure silver by removing the anode and subjecting it to further electrolysis in the opposite direction by making the silver-silver bromide element the cathode in a caustic soda or potash solution of a strength of from one per cent or less to a concentrated solution. In this second or secondary electrolysis we may employ an anode such as graphite, a noble metal or the like. The current density employed may be within the range employed in the first electrolysis and after electrolysis has continued for a short period it will be found that the bromine has been split off from the silver, leaving substantially pure silver upon the cathode, sodium or potassium bromide being formed in solution. The sodium or potassium bromide thus produced may be concentrated and employed as desired, while the silver cathode may be withdrawn and used as an anode in further primary electrolysis of spent developers.

It will be apparent that considerable variation from the details above given may be employed by those skilled in the art, but that such equivalents are intended to come within the scope of the claims appended hereto and forming a part hereof.

What we claim as our invention and desire to be secured by Letters Patent in the United States is:

1. The process of rejuvenating spent photographic developers containing soluble bromides in solution which comprises subjecting such developers to electrolysis in which a silver anode is employed until substantially all of the bromine has been deposited upon the anode of the electrolytic system.

2. The process of rejuvenating spent photographic developers containing soluble bromides in solution which comprises subjecting such developers to electrolysis in which a silver anode is employed until substantially all of the bromine has been deposited upon the anode of the electrolytic system and the bromine has combined with silver of the anode to form silver bromide.

3. The process of rejuvenating spent photographic developers containing soluble bromides in solution which comprises subjecting such developers to electrolysis with a silver anode until bromine is deposited upon and combined with silver of the anode and then subjecting such silver bromide-coated element as the cathode to electrolysis in the presence of a caustic solution.

4. The process of rejuvenating spent photographic developers containing soluble bromides in solution which comprises subjecting such developers to electrolysis with a silver anode until substantially all of the bromine is deposited upon and combined with silver of the anode and then subjecting such silver bromide-coated element as the cathode to electrolysis in the presence of a caustic solution until substantially all of the silver bromide has been reduced to metallic silver.

5. The process of producing silver which comprises subjecting an element coated with silver bromide, as the cathode, to electrolysis in a caustic solution.

6. The process of producing silver which comprises subjecting a silver element coated with silver bromide as the cathode, to electrolysis in a caustic solution until substantially all of the silver bromide is reduced to silver.

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