

[54] **RECOVERY OF SILVER FROM PHOTOGRAPHIC PROCESSING SOLUTIONS**

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[58] Field of Search **423/561, 48, 42; 75/109; 423/37; 23/305**

[56] **References Cited**

UNITED STATES PATENTS

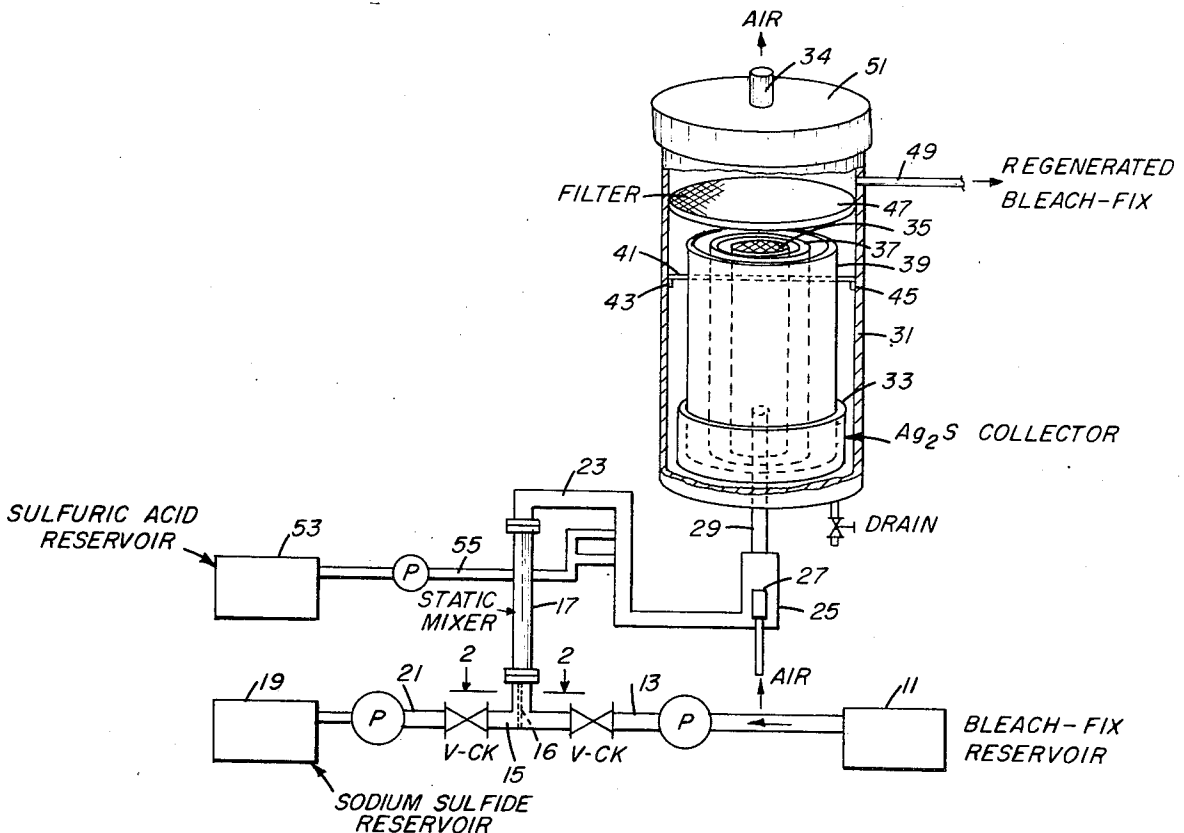
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[57] **ABSTRACT**

Silver is recovered from an exhausted photographic fix or bleach-fix solution by bringing together just at the entrance of a static mixer a stream of a sodium sulfide solution and a stream of fix or bleach-fix solution, and passing the mixture at high velocity through the static mixer, wherein it is repeatedly divided and changed in flow pattern, to precipitate silver sulfide particles. The flowing mixture containing silver sulfide particles is then passed into a separation chamber of enlarged cross section, and its flow is slowed and reversed by baffles to cause the silver sulfide particles to drop out and collect in the bottom. A fix solution is regenerated for reuse by the above procedure. When a bleach-fix is treated, it can be regenerated by introducing air, either upstream or downstream of the separation chamber, to reoxidize to ferric ions any ferrous ions present as a result of the bleaching operation, or those ferrous ions produced by reaction of sodium sulfate with residual ferric ions in the exhausted bleach-fix. A small amount of acid also should be added to adjust the pH to below 7.

5 Claims, 3 Drawing Figures



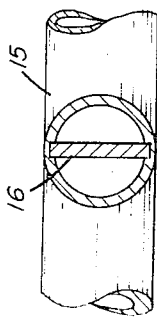
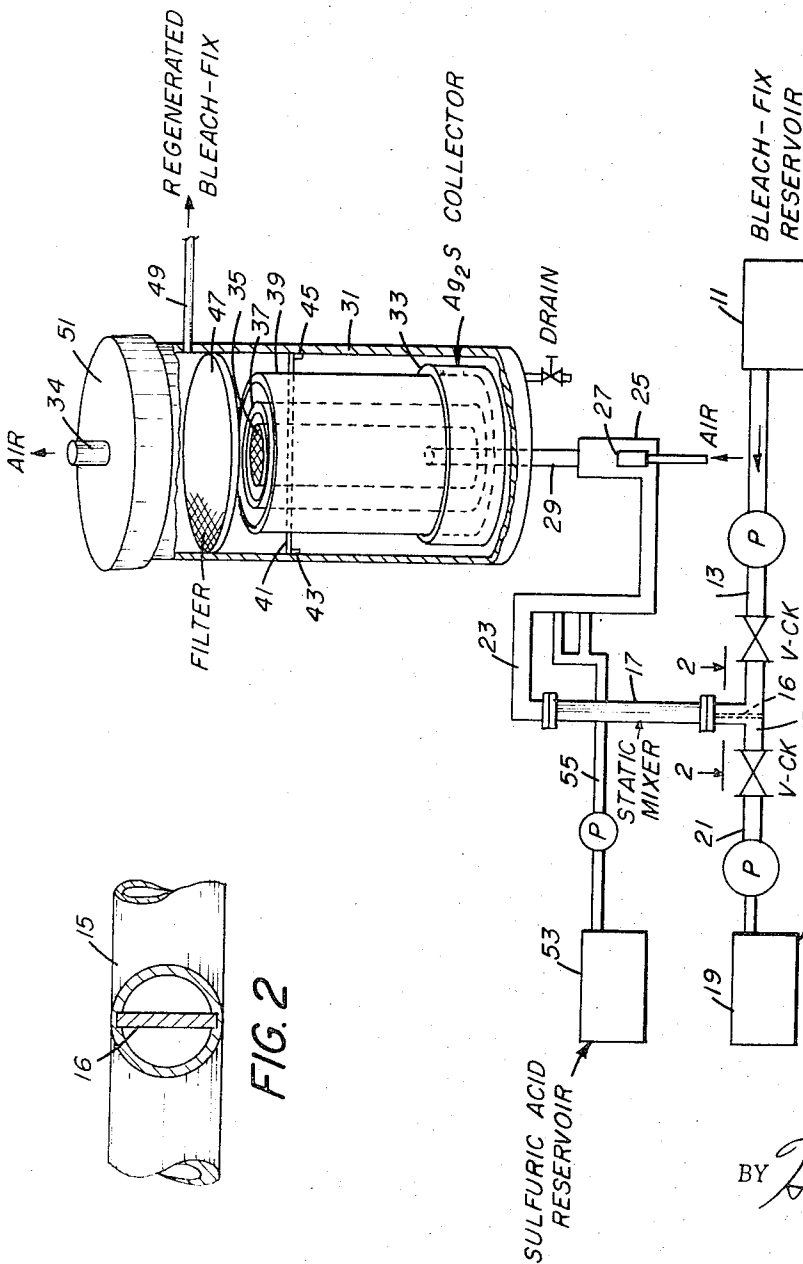
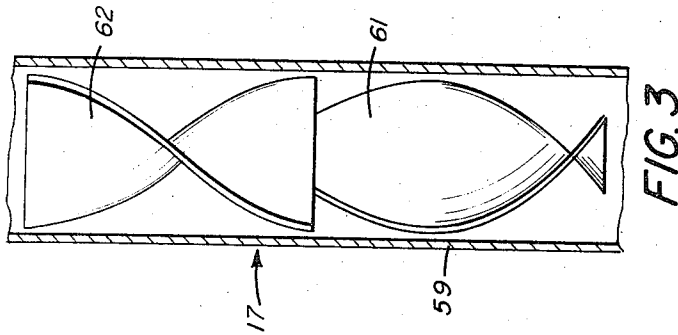


FIG. 2

FIG. 1

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RECOVERY OF SILVER FROM PHOTOGRAPHIC PROCESSING SOLUTIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a novel method of and apparatus for recovering silver from exhausted or spent photographic processing solutions such as a photographic fix, or a photographic bleach-fix solution. Regeneration of the solutions is also accomplished by the invention.

2. The Prior Art

The recovery of silver from spent photographic fixing solutions has been proposed in U.S. Pat. Nos. 1,446,405 and 1,545,032 by treating the fix with a soluble sulfide, such as sodium or potassium sulfide or hydrosulfide, to precipitate the dissolved silver compounds as silver sulfide which is then recovered for later reduction to silver metal. Such fixing solutions commonly are aqueous solutions of sodium or ammonium thiosulfate which is known to the trade as "hypo." Simultaneously with the recovery of silver sulfide, the fixing agent is regenerated and can be reused for fixing developed photographic film and paper.

In recent years the fixing solution has been combined with a bleaching solution so that the fixing and bleaching of a photographic film or paper can be performed in one operation. In such a bleach-fix solution the fixing compound again comprises sodium or ammonium thiosulfate, and the bleaching compound generally comprises ammonium ferric EDTA (ethylenediamine tetraacetic acid). U.S. Pat. No. 3,241,996 describes such a bleach-fix. When the bleach-fix solution has become spent or exhausted most of the ferric ion has been converted by reduction to ferrous ion so that the remaining solution cannot be reused as a bleach-fix but must be discarded. Discarding a used bleach-fix solution is often economically unprofitable, and discarded solution may constitute a pollutant.

Bleach-fix solutions to which the method of this invention is applicable are solutions comprising a water-soluble thiosulfate which serves as the fixing agent. As is well known, thiosulfates which are useful for this purpose include ammonium thiosulfate and alkali metal thiosulfates such as sodium thiosulfate and potassium thiosulfate.

Ferric salts of aminopolycarboxylic acids are included as bleaching agents in bleach-fix formulations. Illustrative examples of the aminopolycarboxylic acids are the following:

- nitritotriacetic acid,
- ethylenediamine tetraacetic acid,
- diethylenetriamine pentaacetic acid,
- ortho-diamine cyclohexane tetraacetic acid,
- ethylene glycol bis(aminoethyl ether) tetraacetic acid,
- diaminopropanol tetraacetic acid,
- N-(2-hydroxyethyl)ethylenediamine triacetic acid,
- ethyliminodipropionic acid.

The ferric salts of aminopolycarboxylic acids utilized in the practice of this invention may be salts in which all cations are the ferric ion, or salts in which one or more of the carboxyl groups have formed a salt with a cation other than iron, e.g., with ammonia or with an alkali metal ion. An example of such a salt is sodium ferric ethylenediamine tetraacetate. The bleach-fix

may also contain a non-chelated salt of an aminopolycarboxylic acid, e.g. the tetra sodium salt of ethylenediamine tetraacetic acid, in addition to the ferric salt.

While the above described fixing agents and bleaching agents are the essential components of bleach-fix formulations to which the method of this invention is applicable, the bleach-fix solutions will usually also include other addenda known to the art to be useful for incorporation in bleach-fix formulations. Thus, for example, they may include an additional silver halide solvent such as water-soluble thiocyanate, e.g., ammonium thiocyanate, sodium thiocyanate or potassium thiocyanate, as well as such compounds as ammonium bromide, alkali metal bromides, amines, sulfites, mercaptotriazoles, etc. The concentration of thiosulfate in the bleach-fix solution is typically from about 5 to about 200 grams per liter and the concentration of the ferric salt of an aminopolycarboxylic acid is typically from about 5 to about 200 grams per liter.

The silver recovery procedures of the prior art are operative, but the treatment is slower and less efficient than desired and a considerable excess of the soluble sulfide is required to recover most of the silver in the solutions. For example, in bench top experiments wherein spent bleach-fix was treated in beakers, it was found that between 4 and 8 times more aqueous sodium sulfide was required for 100 percent silver recovery than was required stoichiometrically. Such an excess raises the pH unduly. Furthermore, the fact that spent bleach-fix solutions containing ferrous ion must be discarded after recovery of silver compounds therefrom creates a problem in their disposal since iron compounds are undesirable in the fresh water of streams and lakes. Moreover, such sulfide treatment in the past has been accompanied by the generation of an unpleasant sulfide odor.

SUMMARY OF THE INVENTION

The above disadvantages of the prior art are overcome by our novel method of treatment which embodies improvements on the prior art chemical reactions for recovering silver from an exhausted photographic fixing solution by mixing and reacting a first flowing stream of fixing solution with a second flowing stream of an aqueous sulfide solution to precipitate silver particles, and separating the precipitated particles and the residual solution from one another.

Our novel improvements comprise bringing the first and second flowing streams together just at the entrance of a static mixer, for extremely efficient mixing. In an elongated mixing zone within the static mixer the streams flow at high velocity and are repeatedly divided and changed in their flow pattern to precipitate silver sulfide particles. Then a third stream comprising the mixed solutions and suspended silver sulfide particles is introduced into the bottom of a separation chamber having a much greater cross sectional area than the third stream so as to reduce flow velocity and permit silver sulfide particles to drop out of suspension. This action is assisted by abruptly reversing the flow of mixed solutions in the chamber, and collecting settled silver sulfide particles in the bottom, after which residual solution having greatly reduced silver content is removed from the top or side of the chamber.

When the exhausted photographic solution is a bleach-fix solution containing ferrous ions, our novel method also comprises regenerating the bleach by in-

roducing oxygen into the mixed bleach-fix and sulfide solutions to convert the ferrous ions back to ferric ions in the residual solution which is then recovered for reuse as bleach-fix, thus obviating the disposal problem. This can be done either upstream or downstream of the separation chamber, or even in the chamber. Before the regenerated solutions can be reused, a pH below 7 is required, and this is accomplished by introducing an acidic solution into either the mixed solutions before separation of silver sulfide, or into the residual solution after it is removed from the separation chamber. When the acidic solution is introduced into the mixed solutions prior to removing them from the separation chamber, the liberation of objectionable ammonia fumes from the residual solutions is also precluded, since ammonia may tend to be liberated above pH 8.

The apparatus for performing the foregoing method steps will be described in more detail hereinafter.

THE DRAWINGS

FIG. 1 is a schematic side elevational view, partly broken away and in section, showing apparatus for recovering silver in accordance with principles of the invention;

FIG. 2 is a cross sectional view of a part of the apparatus, taken along the line 2—2 in FIG. 1; and

FIG. 3 is an enlarged vertical sectional view, partly in side elevation, showing a part of a static mixer of the type used in the apparatus of FIG. 1.

THE PREFERRED EMBODIMENTS

Referring to FIG. 1, a continuous silver recovery and regeneration system will be described. An aqueous spent bleach-fix solution in a reservoir 11 is pumped through a conduit 13 to one cross arm of a pipe tee 15 where it strikes a baffle or partition 16 in the perpendicular leg of the pipe tee, and then enters the bottom of a vertical static mixer 17 (which could also be operated in a non vertical position). Concurrently, aqueous sodium sulfide solution from a second reservoir 19 is pumped through a conduit 21 into the other cross arm of pipe tee 15 and is diverted by partition 16 into the static mixer 17. Thus, the two solutions are kept separate until just as they enter the static mixer, thus avoiding the precipitation of silver sulfide in the approach conduits.

Other soluble sulfides, such as potassium sulfide, can be employed, but sodium sulfide is preferred because it is most stable, easily dissolves in water, contains the highest percentage of sulfide (24.5 percent as sulfide ion), and has the least objectionable odor.

The two solutions then mix intimately together as they flow at high velocity through static mixer 17 to cause the precipitation of silver sulfide particles which are carried along in a suspension with the rapidly flowing highly agitated liquid. The suspension then leaves the static mixer through a conduit 23 and enters an aeration chamber 25 having a nozzle or discharge tube 27 (such as a porous polyethylene gas dispersion tube) for the introduction of air. When treating a used fix solution, air introduction is not necessary; but with a bleach-fix solution air is necessary for oxidizing the ferrous ion to ferric ion. This oxidation becomes progressively more difficult as larger excesses of sulfide are introduced above twice the stoichiometric amount to recover all silver. An air flow rate of 40 liters per minute

is employed to assure the presence of a substantial excess of oxygen beyond that actually required for converting all ferrous to ferric ion.

Then the liquid carrying suspended silver sulfide particles flows through a vertical stand pipe 29 into a separation chamber 31 having a considerably greater diameter than the conduit 29 so that the velocity of flow is reduced sufficiently to permit silver sulfide particles to drop out of suspension and be collected in a shallow pan 33 in the bottom of the chamber. Excess air is bled off through a tube 34 at the top of the chamber which can be vented outside to dissipate odor.

Collection of silver sulfide is assisted by the presence of a central cylindrical baffle 35 having a closed top and an open bottom, and by one, two or more other cylindrical baffles such as 37 and 39 which are concentric with baffle 35, and are open at both top and bottom. All baffles can be of rigid polyvinyl chloride or other corrosion resistant material. The lower ends of all three baffles are positioned within and near the top of pan 33; and all baffles are suspended in the chamber by a transverse rod 41 which is removably and replaceably supported by diametrically opposite bosses 43 and 45 on the inside wall of the chamber. Other mechanical means of suspending the baffles, such as hooks may be used.

The regenerated liquid, which is essentially free of silver sulfide particles, then passes up through a filter 47 removably and replaceably positioned within the chamber (to collect any residual silver sulfide particles), and then passes off through a conduit 49 to a suitable collecting vessel where makeup chemicals may be added.

When enough silver sulfide has collected in the pan 33, a cover 51 is removed from chamber 31, and filter 47 and the concentric baffles are all withdrawn through the open top of the chamber. Then the pan 33 containing silver sulfide particles is withdrawn and emptied, after which the apparatus can be reassembled in reverse order for further operation. Alternatively, the chamber can be constructed such that the bottom portion containing the pan is removable by disconnecting the conduit 29, after which the sulfide is removed from the pan 33.

Before the bleach-fix solution can be reused it must be acidified, as by reducing the pH from 7.5 to 6.8. This can be accomplished by bleeding aqueous sulfuric acid from a reservoir 53 through a conduit 55 to the conduit 23. Alternatively, the acid can be introduced after the solution has left chamber 31 through conduit 49.

While any static mixer 17 which provides high velocity and violent agitation can be used successfully, we have employed a static mixer of the type described in U.S. Pat. No. 3,286,992 which, as partially shown in FIG. 3, comprises an outside conduit 59 within which are located a series of "bow tie" shaped blades or elements comprising flat pieces of metal twisted at 180° in alternating directions and shrink fitted inside tube 59 so there is no gap between blade and tube at any point. Each element 61, 62 etc. divides the stream received from the preceding element in half. We have used successfully a static mixer containing 21 elements, within which the entering mixture is split over 2 million times between entrance and exit, with a continual reversal of the circular direction of flow because of the opposite twist of successive elements.

In practice the sodium sulfide solution should have a strength between about 2 and 3 times the amount stoichiometrically required to precipitate all of the silver present in a spent fix or bleach-fix solution. This is partially due to a reaction of the sodium sulfide with ferric ion present in the EDTA complex of a bleach-fix solution.

The holding time in chamber 31 can vary between several minutes to more than 85 minutes, depending on the dimensions of the unit, the nature of the solution, and the concentration of reactants, particularly the concentration of ferrous ion which must be reoxidized to ferric ion in a bleach-fix solution by controlled bubbling of air through the desilvered solution.

The principles of the invention will become more apparent from the following examples.

Example I

A bleach-fix solution is supplied at 450 ml/minute to tee 15 and is regenerated in the described manner with the static mixer 17 in a horizontal position, while injecting air at 40 liters per minute and adjusting the pH to below 7 with 3.6 N aqueous sulfuric acid flowing at 12.5 ml/minute. A highly concentrated aqueous sodium sulfide solution is supplied to tee 15 at sufficient strength and a flow rate of 12.5 ml/minute to provide 2.5 times the amount of sodium sulfide stoichiometrically required to precipitate all of the silver in the bleach-fix. The high strength and low flow rate prevent excessive dilution of the bleach-fix solution. Before regeneration the bleach-fix contains 3.88 grams of silver per liter, and after regeneration contains only 0.50 gram of silver per liter. Thus, 87.1 percent of the silver has been removed as silver sulfide.

Chamber 31 is 8 inches in diameter and 48 inches long, has a volume of 38.7 liters, and is constructed of rigid polyvinyl chloride. Standpipe 29 is 4 inches long and one-half inch inside diameter, and is threaded into the bottom center of chamber 31.

Example II

A bleach-fix solution containing 4.78 grams of silver per liter is regenerated using a vertical static mixer and aeration, but without pH adjustment. After regeneration the effluent contains only 0.19 gram of silver per liter, for 96.0 percent silver removal. The sodium sulfide solution is supplied in strength and flow rate sufficient to provide 2.1 times the stoichiometric amount for full silver recovery.

The procedure and apparatus described in detail above permit rapid and efficient operation, with considerably less sodium sulfide being required than was previously the case. This reduces the possibility of undesirable sulfur compounds forming in side reactions, such as occur with a large excess of sodium sulfide, which could alter the bleach-fix characteristics. Moreover, there is very little unpleasant odor from sodium sulfide because of the essentially closed design of the apparatus. The fix and the bleach-fix are regenerated and can be reused, instead of having to be discarded with resulting undesirable pollution of fresh water. Furthermore, there is no clogging of the apparatus with silver sulfide particles. Another important feature is that acidification of the stream avoids the release of ammonia gas, which may occur at alkaline pH.

The operation described above is continuous, with overflow spent bleach-fix solution from a film processor continuously entering the system, and regenerated bleach-fix continuously leaving. The principles also apply to batch type operation wherein a tank of spent bleach-fix is accumulated and then passed through the system with the operation being discontinued between tanks. Also, the sulfide and bleach-fix solutions can be introduced through a common dual-headed metering pump to maintain the ratio of flow rates constant. A triple-headed metering pump may be used to simultaneously meter the sulfide, acid, and bleach-fix solutions to maintain a constant flow ratio. Finally, the pH of the solution may optionally be controlled by an automatic pH sensing and controlling device which actuates the acid metering pump when the pH of the solution inside the chamber rises excessively.

The air may alternatively be introduced into static mixer 17, which may be separate as shown, or may actually be used in place of standpipe 29 for compactness.

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.

We claim:

1. In a method for recovering silver from an exhausted photographic fix solution or bleach-fix solution by mixing and reacting a first flowing stream of said solution with a second flowing stream of an aqueous sulfide solution to form silver sulfide particles and separating the particles of silver sulfide and the residual solution from one another, the improvement comprising:

bringing said first and second flowing streams together while they are flowing at high velocity within an elongated mixing zone and repeatedly dividing the flowing fluid and changing the flow pattern thereof within said mixing zone, whereby reaction occurs between said first and second flowing streams to form silver sulfide particles suspended in the flowing fluid; the amount of sulfide in said second flowing stream being at least about twice the stoichiometric amount required to precipitate all of the silver in said first flowing stream;

and directing the stream of flowing fluid leaving said mixing zone into a separation zone in which the direction of flow is abruptly reversed so as to cause the particles of silver sulfide to settle out of suspension.

2. A method as claimed in claim 1 wherein the aqueous sulfide solution is a solution of sodium sulfide.

3. A method as claimed in claim 1 wherein the amount of sulfide employed is from about two to about three times the stoichiometric amount required to precipitate all of the silver in said first flowing stream.

4. A method as claimed in claim 1 wherein the solution from which silver is recovered is a fix solution containing a thiosulfate fixing agent.

5. A method as claimed in claim 1 wherein the solution from which silver is recovered is a bleach-fix solution containing a thiosulfate fixing agent and a bleaching agent which is a ferric salt of an aminopolycarboxylic acid.

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