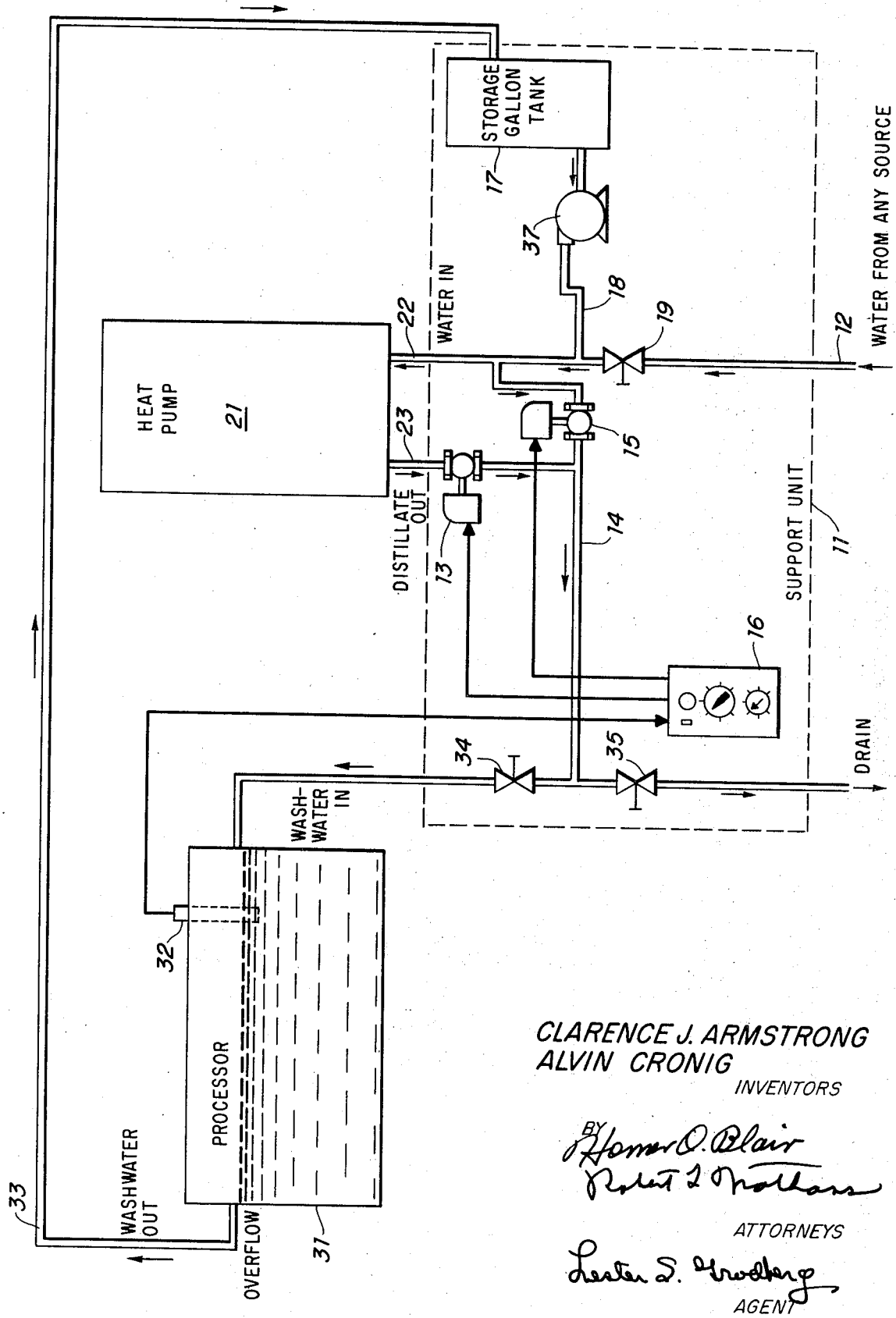
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METHOD AND APPARATUS FOR WASHING OF PHOTOGRAPHIC MATERIAL

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METHOD AND APPARATUS FOR WASHING OF PHOTOGRAPHIC MATERIAL

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ABSTRACT OF THE DISCLOSURE

A method and apparatus for the control of the contamination level of photo wash water supporting an environment for ionic substitution of simple thiosulfate salts in the water with complex argento thiosulfates on the photographic emulsion surface. A water purifier is placed in closed loop with the wash tank to control the level of contamination.

BACKGROUND

Field of the invention

The present invention relates to a method and an apparatus for washing of developed photographic material and more particularly to such method and apparatus wherein the contamination content of the water is maintained within predetermined levels.

Description of the prior art

In silver halide photographic processing systems, the surface of the photographic material as it leaves the developer bath and enters the fixing bath, includes metallic silver in the developed areas of the image, and silver halide in the undeveloped areas. A chemical reaction takes place in the fix bath in which the silver halide forms complex salts such as the argento complexes. Also, free silver liberated from the emulsion of the photosensitive surface is introduced into the fixing solution. The amount of free silver in the photographic fixing solution is directly related to the amount of film that is passed through the solution. Hence, as the film footage increases, the amount of metallic silver in the solution increases and more silver is available to react with the emulsion on the surface of the photographic material, resulting in heavier or more complex argento compounds. These compounds and the simple salts on the surface of the film must be removed to eliminate staining, spotting and fading of the finished photograph. The heavier or more complex the salt with the emulsion, the more difficult it is to remove the compound from the material surface.

In the prior art, it has been common practice to wash the film with large quantities of water for extended periods of time to remove these salts. The obvious disadvantage of protracted washing is that the emulsion tends to swell and distort as it is subjected to more and more water, thus distorting the photographic image. In many uses of the image for precise measurement and maximum information retrieval, such as photogrammetry and reconnaisance, the distortion due to prolonged or uncontrolled washing reduces or eliminates the precision and retrieval capability. Further as the emulsion becomes softer, it absorbs a good deal of water, increasing drying time of the material. Prolonged drying or drying at elevated temperatures necessitated by over-washing further compounds the image distortion problems.

Most commercial photographic processing plants are located in areas of high population concentration. For example, the motion picture and television industries in

the United States are located in Los Angeles, Chicago, and New York city. As years go on, more concern is shown for water conservation and purification. Indicative of the purification problem is concern over the disposal of contaminated solutions into sewerage systems. Also, in many tactical military situations film processors are placed in locations where water supplies are rather limited. Often the water is unfit for any use, particularly photographic washing. Therefore, much effort has been directed toward photographic processing systems incorporating closed loop water reclamation systems in attempts to minimize clean water requirements. In such systems water from the wash bath is cycled through water purification apparatus and returned to the wash bath in a purified state. As has been disclosed above, prior art systems have used considerable quantities of water. Therefore, such reclamation systems necessitate large storage tanks and reclamation or purification systems, capable of processing great quantities of water. Such purification systems are characteristically cumbersome and overly expensive, generally unfit for tactical and commercial applications.

SUMMARY OF THE INVENTION

The present invention provides a method and an apparatus for drastically reducing the amount of wash water to which it is necessary to subject photographic material. By carefully controlling the contamination level of the wash water, it is found that an ionic exchange occurs between complex salts in the photographic material and simple salts in the wash water. Since it is much easier to remove the simple salts than the heavy ones, providing an environment for ionic exchange effects a substantial economy of water and drastically reduces washing time. The surface of the emulsion is not subjected to the distortion mentioned hereinabove. Also drying time is greatly decreased. This is due not only to the fact that the amount of water to which the material is subjected to decreases, but is also due to the fact that the hardness of the emulsion can be kept in its natural hard gel state. This is effected because of the ease with which the simple salts are removed from the emulsion and because the pH of the water is kept within closely controlled limits at the iso-electric point of the gelatin. The simple salt in the water counteracts the acetic acid carried into the wash tank from the fixing bath.

To further reduce the quantities of water used, a closed loop water reclamation system may be utilized. Since the levels of contamination of the water are controlled as described above and either only a portion of the water need be purified in the cycling operation, or only partial purification of the water takes place, an unobvious and unexpected advantage occurs by utilizing the ionic exchange concept described above in a closed loop system. An advantage of ionic exchange is that the amount of water used is drastically reduced, because the water does not have to be pure. In fact, it is undesirable to completely purify the water. Thus only a partial purification of the water is necessary, or alternatively, the purification process does not have to be complete or extremely efficient. The storage facilities, reservoirs and purifiers are reduced in size. The total volume of water necessary to operate such a system is greatly reduced over the closed loop reclamation systems of the prior art.

An object of the present invention is the provision of a method and apparatus for achieving high quality photographic images.

Another object of the present invention is the provision of a method and apparatus for rapid photographic processing.

Yet another object of the invention is the provision of apparatus and a system for photographic processing

wherein the quantities of water utilized are significantly reduced.

Still another object is the provision of a closed cycle photographic washing system enabling disposal of wash water in an uncontaminated state.

Other objects and provisions of the invention will become more fully understood in light of the following specification taken in conjunction with the sole figure of drawing which illustrates in schematic form, a closed loop photographic water reclamation system.

DESCRIPTION OF THE EMBODIMENTS

Throughout the following specification, we will allude to the processing of photographic film. It should be carefully understood that this is merely illustrative and any photographic materials may be processed by the practice of the method and use of the apparatus of this invention. It is intended that this invention be limited only by the scope of the appended claims.

In the processing of silver halide photographic film, it is very common to use sodium potassium and ammonium salts throughout the various baths of the developing process. Sodium sulfite (Na_2SO_3) or potassium metabisulfite ($K_2S_2O_5$) are commonly used as a preservative to prevent aerial oxidation. In the fixing bath sodium or ammonium thiosulfate, $Na_2S_2O_3$ or $(NH_4)_2S_2O_3$, is used to dissolve the silver halides in the unexposed portion of the image on the film. The reaction between the silver halides and the simple thiosulfate salts yields argento thiosulfate complexes which remain entrapped in the emulsion. Examples of such thiosulfate complexes are $Na_2AgS_2O_3$ and $(NH_4)_2AgS_2O_3$. As the amount of film processed through the fixer bath is increased, the amount of silver carried on the film from the developer bath to the fixing bath is increased, thus more free silver is available to form these argento complexes. As the fixing solution becomes older, heavier or more complex, argento salts are formed on the emulsion. Various polythionates such as sodium tetrathionate $Na_2(Ag)S_4O_7$ may be formed. As mentioned herein before, the more complex or the heavier the salt carried by the emulsion into the washing bath, the more difficult it is to remove these salts. We have found that by carefully controlling the contamination, that is, the percentage of soluble contaminants including the simple thiosulfate salt in the wash water, we may create a favorable atmosphere for ionic exchange. Water containing very low concentrations of dissolved salts does not wash as effectively as those containing moderate to high concentrations of dissolved salts in the water. Also, above a certain level of contamination, the wash water will not remove thiosulfates from the emulsion in any measurable degree.

Although the ionic exchange is dependent upon the percentage of simple thiosulfate salt in the wash water, the contamination levels mentioned throughout the specification and recited in the claims refer to the total level of contaminants dissolved or soluble in the wash water and not to simple thiosulfates alone. It has been found by empirical methods that the total concentration of soluble contaminants disclosed contain simple thiosulfates in proportions which create a favorable atmosphere for ionic substitution. The ability to measure the total soluble contamination levels, rather than measuring the level of simple thiosulfate salt greatly simplifies the sensing equipment.

It is quite obvious that the ratio of simple thiosulfate salt to the total soluble contaminant will not remain constant over a protracted period of use of any photoprocessing equipment. However, we have noted in various test runs and throughout long periods of actual practice of the invention, examples of which are presented below, that this factor is of no concern and may be neglected for all practical applications within our experience. Nevertheless, if the complex salts become a problem, a very simple expedient for the removal of gross thiosulfate complexes from the water is available. The chemical addition of suitable reagents to precipitate the sulphur from the thiosulfate complex and filtration of the sulphur from the water will remove the contaminating substances.

To explain the ion exchange theory advanced herein, it is found that if an emulsion containing the thiosulfate ion is considered to be an anion exchange resin, and is made basic by the addition of suitable chemicals, an ideal solution for anion exchange exists where

$$R_2S_2O_3 + 2OH^- \rightarrow 2ROH + S_2O_3^=$$

However, when relatively pure water is presented to the thiosulfate bearing emulsion, no ion exchange can be expected because only a few sulfate ions are present in the wash water. Thus by leaving a predetermined quantity of contamination in the wash water, the thiosulfate ions will exchange with the argento polythiosulfate radicals present in the argento polythiosulfate complexes on the film, leaving thiosulfate salts which are readily removed from the surface of the film. Obviously, if the contamination level of the water is above a particular limit which depends upon the efficiency of the washer, the ionic exchange reaction ceases and the argento thiosulfates will remain in the emulsion.

The prior art references disclose pre-wash hypo eliminating solutions containing sulfites, such as ammonium and sodium sulfite. This invention eliminates the need for any pre-wash conditioning. There are two obvious advantages to the elimination of a wash conditioner or hypo eliminator bath. Firstly, the film processing time is decreased by the elimination of one step in the wash cycle and the size, weight and efficiency of the equipment is also decreased. Additionally, since the sulfite salts are neutralized, acetic acid in the hypo will increase the pH of the wash bath. In the present system, the acidity of the fixer is counterbalanced by the basic pH of the thiosulfates; thus we are able to keep the pH of the film emulsion at a level between 4.7 and 4.9. This has been found to be the "natural" gel point or isoelectric point of the film. Less water, therefore, is absorbed by the gel. Hence the quality of the photograph is enhanced by decreasing the wash time, by decreasing the drying time and by lowering the pH of the wash bath. The combination of these factors enables us to achieve archival quality of films; that is, the films processed utilizing the method and apparatus of the invention, are of as high quality as the photographic properties of the film allow. No distortion occurs due to gelatin swelling, displacement or scratching of the surface of the emulsion.

Since the water is never completely purified, the lower limit of contaminant being approximately 80 parts per million and the upper limit being of the order of 10,000 parts per million, this invention particularly adapts itself to utilization in a closed loop system of water reclamation. In one apparatus used we have found that only one part of clean water is necessary in the recycling operation for every seven parts of contaminated water.

Turning now to the sole figure of drawing, a photo processor washing apparatus **31** is connected in closed loop to a water processor or purification apparatus **21** through a wash water support unit **11**.

Water from an indigenous source (not shown) passes through the support unit **11** via input line **12** and line **22** to a water processor or purifier such as heat pump evaporator **21** where the water is purified. The purified water exists from the processor **21** via output line **23** and solenoid mixing valve **13** to line **14**. Input line **12** also supplies indigenous water to line **14** via solenoid operated mixing valve **15**.

Line **14** is connected to the washing unit **31** of a photo processor (not shown) having a contamination sensor **32** mounted therein. The sensor **32** is connected to a contamination control instrument **16** in support unit **11** which controls the mixing valves **13** and **15**.

Processor wash tank **31** has an output or overflow pipe **33** which is connected to a storage tank **17** in the support

unit 11. Line 18, leads from the storage tank 17 to the mixing valve 15 via a pump 37. Water from wash tank 31 is fed into storage tank 17, a portion of the water from tank 17 is passed to purifier 21 via line 22 and a portion to line 14 via mixing valve 15. Mixing valves 13 and 15 control the ratio of pure to contaminated water.

Once the system is filled, a valve 9 is closed and the system operates in closed loop. The ratio of pure to contaminated water is sensed by sensor 32, which transmits a signal to control 16 which in turn operates the valves 13 and 15 to control the level of contamination of the water. The control 16 is shown as a variable control and may be set an any desired contamination level.

If it is desirable to flush or drain the system, valves 34 and 15 are closed, and valves 35 and 13 are opened. Thus, the system may be drained with all of the water passing through purifier 21. With this arrangement, all of the water flushed from the system will be pure and the possibility of contaminating an indigenous supply is eliminated.

In a particular embodiment it was found desirable to use a flash evaporator or heat pump as the purification unit 21. The major advantage of such a system are that the unit is relatively small and compact. As is well known, a flash evaporator lowers the pressure inside the unit below the ambient level of pressure and thus the temperature of the solution to be purified does not have to attain atmospheric boiling temperature. Thus associated refrigeration apparatus necessary is extremely small. Additionally, the use of a flash evaporator facilitates complete purification of the water upon disposal. Further, the flash evapoartor is extremely stable and requires no regeneration as in ion exchange resin systems.

It should be obvious, however, because of the quantity of water utilized in this system due to the level of contamination of water which is found to be desirable, that any purification apparatus will work and the system as a whole will operate in a manner far superior to that of prior art systems. For example, if a reverse osmosis technique is used, wherein water enters a chamber under high pressure and is then forced through a semipermeable membrane effecting cleanup of the water, no holding reservoirs would be necessary. The effectiveness of the membrane could be designed such that a desired level of contamination would be maintained. The advantage of such a unit is balanced by the disadvantage of disposal of the water upon completion. It is further noticed that with a flash evaporator utilized as the water processor, maintenance is slight. It was found that the water could be used for an indefinite period of time. Additionally, maintenance or cleaning of the scaling on the evaporator may occur only once every six months.

The following examples are indicative of results obtainable by utilizing the method and apparatus of the instant invention.

EXAMPLE I

A heat pump AMF RP–720 manufactured by American Machine and Foundry Corporation of Waterford, Conn. was placed in closed loop as shown in the sole figure of drawing with a Versamat II CM photographic processor manufactured by Eastman Kodak Company of Rochester, N.Y. The developing solution use consisted of:

Water—500 ml.
Monomethyl paramido-phenol sulphate—2.2 g.
Sodium sulfite—96 g.
Hydroquinone—8.8 g.
Sodium carbonate monohydrated—56 g.
Potassium bromide—5 g.
and
Potassium bromide—5 g. and
Add water to make one liter.

This developer is commercially available from Eastman Kodak Company and generally known as Kodak Developer D–19.

The fixer or hypo used consists essentially of

Sodium thiosulphate hydrated—250 g.
Sodium sulphite—10 g.
Glacial acetic acid 1.35 specific gravity—50 cc.

and add water to make one liter. This is commercially available from Eastman Kodak Company and is sold under the trade name of Kodak Rapid Fix (without hardener).

The film processed was Eastman Kodak plus X Aerecon of 5 inches in width. The properties of this film are shown in Eastman Kodak Manual of Physical Properties published by Eastman Kodak Company, Rochester, N.Y., in section 19, type number 8401, March 1963.

The processor was completely flushed, filled with tap water, and allowed to run without film being processed for 35 minutes before processing started.

Time	Soluble Contaminants (p.p.m.) Proc. Output	Proc. input	Dist.	pH Proc. Input	pH Dist.	Resid. Hypo, mg./in.²
Start: 0	1,100	105	60	8.05	10.1	
½ hr	1,100	330	50			
4 hrs	5,500	3,650	190	5.5		
6 hrs	8,000	3,900	270	5.1	4.3	.020
10 hrs	9,500	3,250	210	5.2	4.25	0.30
15 hrs	11,500	2,350	330	5.0	3.8	.015
21 hrs	25,000	4,500	550	5.0	3.7	.040+
30 hrs	24,500	4,400	720	5.2	3.9	.040
44 hrs	25,000	3,400	760	5.5	5.0	.020

NOTES:
Total footage—31,370 feet.
Total water recirculated—9,290 gallons.
Total water to start—25 gallons.
Total water to end—25 gallons.

EXAMPLE II

In this example three Versamat processes of the type used in Example I were connected in parallel with the heat pump and support system shown in the cycle. All other system parameters were the same as they were used in Example I.

Time	Proc. Output	Proc. Input	Dist.	Proc. Output	Proc. Input	Dist.	Resid. Hypo, mg./in.² A	B	C
½ hr	2,500	2,750	200	6.2	5.7	8.8	.020	.020	.30
2 hrs	10,000	8,500	210	5.2	5.0	8.1	.030	.040	.040
5 hrs	8,000	4,900	320	5.0	4.8	3.7	.030	.045	.050
7 hrs	6,000	3,200	420	4.8	4.8	3.8	.020	.020	.030
9 hrs	8,200	4,500	400	4.8	4.6	4.7	.050	.050	.040

NOTES:
Total footage processed (cumulative)—8,972.5 ft.; 9.5″; 1,450 ft. 5″.
Total water recirculated—5446 gallons.
Make up water required—0 gallons.

EXAMPLE III

A single Versamat processor was utilized. Sea water was obtained from Myrtle Beach, S.C. with contamination level of 7,500 parts per million and a pH of 5.4. One hour 25 minutes was required to convert 36 gallons of sea water to 20 gallons distilled water. However, 5 gallons of distilled water, enough to start to utilize the water reclamation system, was obtained in 11 minutes.

EXAMPLE IV

Twenty gallons of swamp water was obtained from an indigenous slough located between Sumter, S.C. and Columbia, S.C. One hour 5 minutes was required to distill this water. Five gallons of liquid were available after 12 minutes. Again, sufficient water to start operation of a

single processor. A single processor as shown in the sole figure of drawing was connected in parallel utilizing the distilled swamp water. The following table illustrates the operation of the system utilizing the distilled swamp water as shown in the table.

Time	Contamination (p.p.m.) Proc. Output	Dist.	Proc. Input	pH Proc. Output	Dist.	Proc. Input	Resid. Thio, mg./in.^{2}
Start	12,000	450	950	4.9	5.7	4.3	
6 hrs	10,000	600	890	4.7	4.4	4.3	
10 hrs	9,500	150	320	5.8	5.9	6.2	.025
15 hrs	9,000	330	500	5.1	4.3	4.4	.015
17 hrs	13,000	350	500	5.2	4.5	4.8	.025
24 hrs	10,000	450	690	5.0	4.3	4.5	.030

NOTE.—Total footage—8,510 feet.

While this invention is especially adapted for use with silver halide photographic processing systems, it will be understood that this invention is equally as useful in any of those photographic systems for which fixing and washing can be applied to chemical development or physical development of latent images where the developed portions of the print comprise metal images and the non-exposed portions comprise metal salts. Examples of photographic systems other than metal halides to which this image can be adapted are those disclosed in U.S. Pat. No. 3,152,903 and abandoned application Ser. Nos. 199,211, filed May 14, 1962, 514,200, filed Dec. 6, 965 and 514,76, filed Dec. 6, 965. Thus the photographic system for which this invention is adapted comprises an oxidizing agent which is usually the image former. The preferred oxidizing agents comprise the inorganic and organic metal salts having reducible metal ions having at least the oxidizing power of the cuperic ion (Cu^{+2}). Examples of such salts are the salts of the reducible metal ions, Ag^{+}, Hg^{+2}, Pb^{+4}, Au^{+3}, Pt^{+4}, Ni^{+2}, Sn^{+2}, Pb^{+2}, Cu^{+2}, and Cu^{+1}.

Thus we find that by practicing the method and using the apparatus of the present invention, the quality of the photographic film or other photographic materials washed is limited only by the characteristics of the photographic material or processes other than washing. Severe constraints which might be placed on the use and disposal of water in the future are virtually eliminated by practice of this invention and additionally, the maintenance problems of the apparatus are significantly reduced over prior art systems.

Various modifications are contemplated and may obviously be resorted to by those skilled in the art without departing from the spirit and scope of the inventor as hereinafter defined by the appended claims.

What is claimed and desired to be secured by Letters Patent of the United States is:

1. In the processing of photographic material including at least the steps of exposing, developing and washing said material with water to remove metal thiosulfate complexes therefrom, the improvement comprising controlling the amount of total soluble contaminents in said wash water during the entire washing operation to an amount of between about 80 p.p.m. and about 10,000 p.p.m., said total soluble contaminents including simple thiosulfates which undergo ion exchange with said metal thiosulfate complexes resulting in more efficient washing.

2. The improvement of claim **1** wherein said photographic material contains a photosensitive metal halide and said developing comprises chemical development.

3. The improvement of claim **2** wherein said metal halide comprises silver halide.

4. The improvement of claim **1** wherein said photographic material contains a photosensitive semiconductor material and said development comprises physical development.

5. The improvement of claim **4** wherein said physical development comprises contacting the photosensitive semiconductor material with a redox system.

6. The improvement of claim **5** wherein said redox system contains a reducible metal ion and an agent capable of reducing said metal ion.

7. The improvement of claim **6** wherein said reducible metal ion comprises silver ion.

8. The improvement of claim **1** wherein said metal thiosulfate complexes are selected from the group consisting of argento polythiosulfate, cuperic polythiosulfate, ferro polythiosulfate, ferric polythiosulfate, mecuric polythiosulfate, mercurous polythiosulfate and combinations of these.

9. The improvement of claim **8** wherein said metal thiosulfate complex comprises an argento polythiosulfate.

10. The improvement of claim **9** wherein said simple thiosulfate salt comprises a member selected from the group consisting of ammonium thiosulfate and sodium thiosulfate.

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