(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 585 792 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **93113548.7**

(51) Int. Cl.[5]: **G03C 5/31**, G03C 5/30

(22) Date of filing: **25.08.93**

(30) Priority: **04.09.92 US 941343**

(43) Date of publication of application:
09.03.94 Bulletin 94/10

(84) Designated Contracting States:
BE DE FR GB IT

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(54) Process of recycling spent photographic developer and recycled photographic developer.

(57) A process for recycling a hydroquinone-free black-and-white photographic developer composition comprises the steps of collecting the developer, optionally filtering the collected material, and reconstituting the developer, whereby the spent developer is brought back to substantially the activity of fresh developer having the same composition wherein the recycled developer can be used to process black-and-white photographic materials without adverse effects.

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BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a process of recycling spent photographic developer compositions wherein the spent developer is collected and reconstituted and can be re-used without detrimental effect on films processed therein.

2. Description of Related Art

Photographic developer compositions are well-known in the art. The development of exposed silver halide photographic elements comprises a multiple step process of development, fixing, washing and optionally a stopping step. The development step is conventionally undertaken with an aqueous alkaline developer composition containing a developer, also known as a developing agent either singly or with one or more additional developing agents. A comprehensive list of developing agents is provided in C. E. K. Mees, The Theory of the Photographic Process, Chapters 14-15, The Macmillan Company (1959, Rev. Ed.) The most commonly used developing agent, particularly for processing black-and-white photographic silver halide elements is hydroquinone. The hydroquinone or other suitable developing agent serves as a strong silver reducing agent to reduce the silver halide grains containing a latent image to yield the developed photographic image.

Hydroquinone-based developer compositions typically contain relatively high levels of sulfite-based components. Also, the pH of hydroquinone-based developer compositions is maintained within strict alkaline ranges with alkaline buffers, such as carbonates, phosphates, borates, etc., either alone or in combination with hydroxides. While hydroquinone-based developer compositions have been successfully employed for many years, recently the use of these conventional developer compositions have been imposed with various guidelines and regulations due to the toxicity and environmental hazards associated with the hydroquinone, sulfite, and other components as well as the alkaline nature of the developer.

Another class of developing agents are disclosed in U.S. Patent 2,688,549, which teaches the use of ascorbic acid and sugar-type derivatives thereof as developing agents in photographic developers. Because ascorbic acid and its derivatives are not considered hazardous to the environment, it is desirable to have developer compositions which use these developing agents. Similarly, U.S. Patent 5,098,819 teaches improved photographic developer compositions which are free of hydroquinone and free of alkali metal hydroxides and which utilize ascorbic acid, derivatives and salts thereof as the developing agents.

Although these ascorbic acid-based developer compositions are more environmentally friendly than hydroquinone-based developers, the nevertheless raise many of the same serious environmental concerns as conventional developers when they are discharged as waste. For example, developer compositions are highly alkaline with pH of at least 9.5, and they may also contain alkali sulfites as antioxidants in approximate amounts from 10% to 100% of the amount of the developing agent. Further, effluents from spent photographic developers have a Chemical Oxygen Demand (COD) of about 70,000 to 100,000 ppm, which exceeds the current limits set by the Environmental Protection Agency and other regulatory agencies. The COD value represents the degree to which a solution will compete with biological systems for the supply of oxygen. Although COD of the developer effluent can be reduced by the addition of more chemicals to diminish the reducing power of the effluent, this is a circuitous solution.

In view of the current environmental concerns surrounding the discharge of spent photographic developer compositions into the environment and the likelihood of increased environmental regulations, it is highly desirable to eliminate or reduce the introduction of the spent developer effluent into the environment by recycling the used developer. Apart from the obvious environmental benefits to recycling, there are also financial advantages to recycling the spent developer due to a reduction in the amount of raw materials needed and in the cost of compliance with environmental regulations.

A major obstacle to recycling, however, is being able to reconstitute the developer such that the performance of photographic materials in recycled developer is equivalent or substantially equivalent to the performance of the photographic materials in fresh developer. Conventional hydroquinone-based developers are poor recycling prospects because the oxidation products of hydroquinone (formed during development of photographic materials) are developing agents themselves and thus contribute to the complexity of the developer composition. The development activity of these oxidation products makes it difficult, if not impossible, to reconstitute spent hydroquinone-type developer compositions to obtain a developer composition having acceptable performance. In addition, the degradation (i.e., oxidation) of hydroquinone produces large, dark (almost black in color) polymeric compounds which are difficult to quantitatively analyze and separate. The presence of these degradation products in developer compositions contributes to sludge formation and staining of photographic elements processed therein.

The present invention is based upon the observation that ascorbic acid-type developing agents produce light-colored oxidation products and the discovery that these products do not affect the performance of the developer composition. It has also been discovered that the presence of these products does not produce undesirable effects (such a staining) to photographic elements processed therein.

SUMMARY OF THE INVENTION

In accordance with this invention, there is provided a process for recycling non-hydroquinone containing black-and-white photographic developer compositions comprising the steps of:

a) collecting the developer; and

b) reconstituting the developer for re-use.

In another aspect, the present invention comprises a recycled black-and-white photographic developer composition made according to the above process.

In a preferred embodiment, the hydroquinone-free black-and-white photographic developer composition comprises:

Ingredients	Amount (grams)
sulfite ion	3 to 30
sequestering agent	1 to 7
bromide ion	1.5 to 10.0
developing agent	20 to 90
secondary developing agent	0.25 to 3.0
antifoggants	0.05 to 0.65
development accelerator	0.01 to 3.0
Water	to make 1 Liter

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

For the reasons noted above, the benefits of the present process are obtained when the developer composition is free of hydroquinone-type developing agents. Non-hydroquinone containing photographic developer compositions are disclosed, for example, in the aforementioned U.S. Patents and in U.S. Patent Application Serial Nos. 07/683,248, filed April 10, 1991 and 07/684,192, filed April 12, 1991, each of which are hereby incorporated by reference in their entirety. All of these references disclose the use of ascorbic acid-type developing agents, which are preferred in the present invention because they produce light-colored oxidation products which do not interfere with development, and thus, can be successfully reused to provide an environmentally sound method of developing photographic materials without detrimental effect on the performance of the photographic materials.

It is contemplated that other developing agents suitable for use in developing black-and-white photographic elements may be employed to advantage in the present invention. To be a successful candidate for recycling, the developing agent must be one which avoids the combination of disadvantages presented by hydroquinone-type developing agents. In other words, it must be one which either (1) does not interfere with the developer activity or produce undesirable effects on photographic elements processed therein; or (2) is readily removed from the spent developer. Because of the complexity of developer compositions used to process color films, they are not considered to be viable candidates for recycling under the present process.

Particularly preferred developing agents which can be employed to advantage in the present invention include (1) ascorbic acid and sugar-type derivatives thereof; (2) stereoisomers and diastereoisomers of ascorbic acid, such as for example erythorbic acid, and their sugar-type derivatives; (3) salts and mixtures of (1) and (2); (4) 2-keto gluconic acid and derivatives thereof, and (5) mixtures of (1) through (4). Example of such compounds include, DL-ascorbic acids, sorboascorbic acid, ω-lactoascorbic acid, maltoascorbic acid, L-araboascorbic acid, sodium ascorbate, potassium ascorbate, sodium erythorbate and potassium erythorbate, 2-keto gluconates, potassium, sodium, ammonium, and methyl derivatives thereof. Most preferred as the developing agents are ascorbic acid, sodium ascorbate, erythorbic acid, and sodium erythorbate.

The developer composition may contain a multitude of conventional adjuvants which serve various functions such as secondary developing agents, antifogging agents, buffers, sequestering agents, swelling control agents, and development accelerators. Such adjuvants are well known to those of ordinary skill in the art. Preferred secondary developing agents are pyrazolidone or metol and derivatives thereof, with 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone and 1-phenyl-3-pyrazolidone being particularly preferred.

Examples of antifogging agents include benzotriazole, phenylmercaptotetrazole, and benzimidazole and derivatives thereof, used alone or in admixture. Soluble bromides, particularly alkali metal bromides (e.g., potassium bromide, sodium bromide) are the preferred restrainers. It is preferred to have both antifoggant agents and a restrainer in the developer. As discussed hereinbelow, it is particularly preferred for the developer to contain from about 7 to about 10 grams/Liter of an alkali metal bromide, whereby a greater percentage of spent developer can be recycled and reused in accordance with the present process.

Small amounts of sequestering agents (or chelating agents) are also generally employed to sequester trace metal ions, e.g., copper and iron ions, present in the water or chemicals used to produce the developer composition and in the films. Preferred sequestering agents are sodium salts of EDTA.

Preferably an antioxidant is also present in the developer composition. Antioxidants are normally used in developer compositions as preservatives, however, such compounds serve the additional function of an accelerating compound in the preferred developer composition disclosed herein. Examples of suitable antioxidants include alkali metal sulfites, bisulfites, metabisulfites and carbonyl-bisulfites adducts. A preferred antioxidant is sodium bisulfite.

The pH of the developer is adjusted into the range of about 9.0 to about 11.0 by adding one or more of an alkali metal carbonate, such as sodium or potassium carbonate; an alkali metal bicarbonate, such as sodium or potassium bicarbonate; and, an alkali metal hydroxide. Preferred are potassium hydroxide and potassium carbonate in a ratio of 2 to 1.

In addition to the above adjuvants, a development accelerator may be included in the developer composition to increase developer activity to that of conventional development times. Inclusion of a development accelerator in the ascorbic acid based developer compositions discussed above renders such compositions equivalent or substantially equivalent in development activity to conventional hydroquinone-based developers for all families of films common to graphic arts, i.e., camera, contact, and photoelectronic (e.g., scanner and imagesetting) films and papers. Developer accelerators suitable for use in this invention include quaternary ammonium compounds and aryl hydrazides, such as those disclosed in U.S. 4,937,160. Because many commercially available films now contain hydrazine or hydrazide compounds as part of the film itself, the preferred development accelerators are the quaternary ammonium compounds disclosed by Pangratz in U.S. Serial Number 07/801,347, the disclosure of which is hereby incorporated by reference. A particularly preferred quaternary ammonium development accelerator is 1-phenethyl-2-picolinium bromide (PPB).

A suitable non-hydroquinone developer composition may comprise:

Ingredients	Amount (grams)
sulfite	3 to 50
sequestering agent	1 to 7
bromide	1.5 to 10.0
developing agent	20 to 90
secondary developing agent	0.25 to 3.0
antifoggants	0.05 to 0.65
development accelerator	0.01 to 3.0
Water	to make 1 Liter

A typical and preferred developer composition will comprise:

Ingredient	Amount (grams)	
	Range	Preferred
Sulfite	10 - 30	15.8
Tri-sodium EDTA	2 - 7	3.5
Potassium bromide	7 - 10	8
Sodium Erythorbate	20 - 60	40
Glucono Delta Lactone	0.1 - 1.0	0.7
4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	0.25 - 1	0.5
Benzotriazole	0.15 - 0.35	0.25
Phenylmercaptotetrazole	0.025 - 0.1	0.05
PPB	0 - 0.5	0.3
Water	to make 1 Liter	

The process of recycling spent photographic developer in accordance with the present invention comprises the steps of collecting the spent developer and reconstituting the spent developer for reuse. As noted, the first step in the process is to collect spent developer. The term "spent developer" as used herein, means a developer composition which has been used to process photographic film or which otherwise has lost some of its development activity as compared to fresh or virgin developer.

The collection step in the present process may conveniently be practiced by collecting developer purged from a developer tank of a processor (such as during processing and/or during automatic replenishment of the developer) in an off-line tank until a sufficient quantity of spent developer is available for the next step. It is to be understood that the process of the present invention does not require any particular amount of spent developer be collected before the reconstituting step. However, for obvious reasons, it is desirable for the present process to be practiced in batch quantities.

It is advantageous and indeed preferred for the collection step to include the separation of liquid developer from any particulate matter present therein. It is not uncommon for spent developer to contain a variety of foreign particulate matter, such as gelatin, conglomerates of silver, hair, dirt, paper clips, etc. The separation of liquid developer from particulate matter may be practiced in any conventional manner, such as by decanting or filtration.

After a convenient quantity of spent developer has been collected, the next step in the present process comprises reconstituting the developer for reuse. By "reconstitute", it is meant that the concentration of the various components in the spent developer is adjusted to obtain the concentration of such components as would be present in fresh developer. The term "fresh developer" denotes a developer which is newly mixed, and/or which has not been used to develop a significant amount of film, and/or which has not been held at elevated development temperatures, i.e., about 95°F to about 110°F, for any extended period of time.

Depending upon the particular developer composition being recycled, the reconstituting step may involve the addition of certain developer components to increase the concentration thereof or the dilution of the spent developer to decrease the concentration of components. More particularly, it is well known that many developer ingredients are wholly or partially consumed during development of photographic elements. Thus, the concentration of such ingredients in spent developer would be lower than the concentration in fresh developer. In the reconstituting step, these ingredients would be added to the spent developer.

On the other hand, it is equally well known that other developer ingredients, particularly bromide ion, may actually be higher in concentration in spent developer than in fresh developer. With bromide in particular, this increase is due to the use of the developer to process films containing silver bromide grains. In such instances, the reconstituting step would involve diluting the spent developer (e.g., with water) to reduce the concentration.

For most applications, both an addition and dilution will be necessary to reconstitute the spent developer. In those circumstances, it may be convenient to combine the addition and dilution steps as may be required by formulating a fresh developer composition which does not contain the particular ingredients which need to be diluted (such as, for example, a bromide-free developer) and adding that composition to the spent developer. In any event, the result of the reconstituting step should be a developer composition that is substantially the same as a fresh developer composition. In the case of ascorbic acid-type developers, the reconstituted developer composition would also contain the oxidation products of the ascorbic acid-type developing agents.

It is particularly preferred for an analysis step to be performed prior to or as part of the reconstituting step. The analysis step, as the name implies, would comprise an analysis of the spent developer to determine the concentration of the various ingredients which are to be reconstituted and the pH. Conventional analytical methods, such as titration, spectroscopy and chromatography, may be used to conduct the analysis of the spent developer. In particular, the spent developer should be analyzed for the concentration of developing agent (both primary and secondary) and antifoggant(s), since these components are usually critical to the performance of a developer.

Based on conventional replenishment rates for developer, it is typically the case that all of the developer components (with the exception of bromide ion) are present in the spent developer from 80% to 90% of their original starting concentrations. The components which are lower in concentration than the original starting concentration of the fresh developer are added to the spent developer in an amount sufficient to achieve original starting concentrations based on the final volume of reconstituted developer.

It may also be necessary to reconstitute other components in the spent developer, such as for example, sequestering agents, swelling control agents, antioxidants, etc., as these components are often necessary for suitable performance of the reconstituted developer. Many of these other components, however, can be reconstituted on a volumetric basis.

As already noted, it may be necessary to dilute the spent developer in order to compensate for the higher concentration of the bromide ion or to compensate for the evaporation losses in the developer due to high temperature processing. It is important to maintain the concentration of the bromide ion due to its restraining effect; the greater the bromide ion concentration, the more the development of film is restrained. The concentration of the bromide ion in the spent developer solution is generally dependent upon the mix of films processed in the developer, i.e., the proportion of the processed films which are totally or partially silver bromide grain films. It should be understood that if all the films processed in the developer are entirely silver chloride grain films, then the spent developer may not need to be diluted to the extent that the spent developer would if some of the films processed contained silver bromide. Another factor which may influence the concentration of bromide ion in the spent developer includes the amount of developed density, i.e., the proportion of the imaged film which is high density and low density.

A typical non-hydroquinone developer composition for black-and-white films will contain from 2 to 3 g/L of bromide ion, which can increase to about 8 to 10 g/L in spent developer. Thus, in reconstituting such developers, it may be necessary to dilute the spent developer from about 70% to about 30% of the collected volume to reduce the bromide ion concentration to acceptable levels. In other words, using conventional developer compositions to process silver bromide films, the recycled developer resulting from the present process would comprise between 30-70% spent developer and 70-30% fresh ingredients.

It has been found that the efficiency of the present process is improved substantially by using a developer composition having a bromide concentration of about 7-10 g/L. Ascorbic acid-type developer compositions in particular are able to tolerate such high levels of bromide. With a high bromide starting level, the additional bromide resulting from film through-put represents a much lower percentage increase in bromide as compared to the more conventional developer compositions. Thus, a lower dilution factor is needed to return the elevated bromide levels to an acceptable starting concentration. In fact, using the preferred developer composition in the present process results in recycled developer comprising from about 70% to greater than 97% spent developer and only up to about 30% fresh ingredients.

After the spent developer has been analyzed and the appropriate additions and dilutions have been effected, the pH of the developer should be adjusted using one or more of the well known adjuvants for that purpose. Preferably, the pH should be between 9.0 and 11.0.

It will be readily apparent to those of ordinary skill that the composition of the recycled developer will not (and need not) be identical to the composition of fresh developer. Indeed, as noted previously, ascorbic acid-type developing agents degrade to light-colored oxidation products. The presence of these products does not interfere with the activity of the recycled developer and they do not adversely affect photographic elements processed therein. Therefor, these oxidation products need not be removed from the recycled developer. Similarly, ingredients such as carbonates and hydroxides, which serve only as pH adjusting and buffering agents, may be substituted with equivalent alkali buffering and adjusting agents in the reconstituting step, so long as the recycled developer has the proper pH and buffer capacity.

Accordingly, it is to be understood that during the reconstituting step of the present invention, it is only necessary for those ingredients essential for the proper functioning of the developer to be adjusted to within their acceptable range for fresh developer.

Photographic developers that have been recycled according to the present process can be used in the same manner as fresh developer solutions, including as a replenishment solution and to initially charge the processor. They may be used in a variety of processing equipment and techniques well known to those skilled in the art.

EXAMPLES

Example 1A

The following is an example of a preferred developer composition prepared and recycled according to the teachings of the present invention. A fresh developer composition was made having the composition as shown in Table A.

TABLE A

Ingredient	Grams/Liter working strength
Tri-sodium ethylene-diaminotetraacetic acid (EDTA)	2
Sodium bisulfite	10
Potassium bromide	3
Erythorbic acid	80
4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	0.5
Benzotriazole	0.5
Phenylmercaptotetrazole(PMT)	0.1
Water	to 1 Liter

The pH of the solution was adjusted to 10.5 using a hydroxide and carbonate buffer solution, (approximately a 2:1 ratio hydroxide:carbonate). The developer solution was placed into the developer tank of a deep tank processor and maintained at 100 °F.

Approximately 250 sq. feet of various types of black-and-white graphic arts films (E. I. du Pont de Nemours & Co., Wilmington, DE) were developed in the processor per week. Films were sensitometrically tested when the processor was initially charged with the fresh developer. The various films were processed in the developer with a 23 second development time. The developer in the tank was replenished with fresh developer solution having the above composition at a rate of 0.25 ml/sq.in. of film processed. Spent developer (developer which was purged from the development tank during processing of the films and/or during replenishment) was collected in an off-line tank until 10 gallons had been collected (approximately 2-4 weeks processing time). The spent developer was filtered with a 10 micron particle size filter to remove particulate matter therefrom.

A sample of the spent developer was analyzed to determine the concentration of potassium bromide, erythorbic acid, Dimezone-S, PMT, and benzotriazole. The concentration of bromide ion was determined using titration. The concentration of erythorbic acid was determined using UV spectroscopy. The concentrations of PMT, Dimezone-S and benzotriazole were determined using high performance liquid chromatography (HPLC). Results of the analysis are shown in Table B.

Based upon the bromide concentration, 5.6 gallons of the spent developer was removed from the off-line tank. To the remaining 4.4 gallons of spent developer, the ingredients were added in the amounts indicated in Table B and enough water was added to bring the total volume up to 10 gallons. The pH was adjusted to 10.5 with hydroxide/carbonate buffer solution. The recycled developer was added as a replenishment solution to the developer tank in the processor. The cycle of processing about 250 sq ft of film per week; collecting spent developer; reconstituting; and reusing the developer was repeated 10 times.

TABLE B

Ingredient	Concentration in Spent Developer	Amount Added to 4.4 gal of Spent Developer
Potassium bromide	6.8 gm/Liter	--
Erythorbic Acid	96% of original level (76.8 gm/L)	1746 g
PMT	67.9% of original level (0.0679 gm/L)	2.65 g
4-hydroxymethyl-4-methyl-1-p-henyl-3-pyrazolidone	91.7% of the original level (0.4585 gm/L)	11.27 g
Benzotriazole	93% of the original level (0.4650 gm/l)	11.17 g

After 10 cycles, the sensitometric performance of films developed in the recycled developer was compared against the sensitometric performance of films processed in fresh developer. A conventional, fresh hydroquinone-containing developer (CUFD; E. I. du Pont de Nemours & Co.) was also included for comparison. Speed, gradient and maximum density (Dmax) were determined for all films and papers in each of the three developers. Results are reported in Table C. Speed and gradient in the reconstituted developer and CUFD are reported as a percentage, using the films developed in fresh developer as the standard.

TABLE C

FILM	EXPOSURE	DEVELOPER	[1]RELATIVE SPEED	[2]RELATIVE GRAD	Dmax
CPR (positive camera speed)	Point source 4 ft. candles, 4 sec	FRESH	100	100	4.3
		RECYCLED	122.5	100	4.2
		CUFD	100	106	4.5
ONF (negative camera speed)	Point source 0.2 ft. candles, 12 sec	FRESH	100	100	5.0
		RECYCLED	95.5	105.8	5.0
		CUFD	103	112	5.3
BLD (bright light positive)	Xenon flash 15 sec	FRESH	100	100	5.8
		RECYCLED	100	102.6	5.6
		CUFD	100	110.5	5.7
BLF (bright light negative)	Xenon flash 15 sec	FRESH	100	100	5.6
		RECYCLED	98.8	92.9	5.2
		CUFD	98.8	96	5.6
CHC (image-setting film)	*10^{-3} sec, with 5 color correction and 0.7 neutral density filters	FRESH	100	100	5.1
		RECYCLED	113	100	5.4
		CUFD	89	96	5.8
CHC-P (paper)	*10^{-3} sec, with 5 color correction and 0.7 neutral density filters	FRESH	100	100	1.6
		RECYCLED	85	90.9	1.7
		CUFD	100	100	1.8

* Exposure on an EG&G Sensitometer, Model PH-11 (Grier Inc.) using a square root of 2 wedge.

[1] Speed was measured at 0.25 density for all films and papers.

[2] Gradient was measured at 0.30 to 0.05 densities for positive films and papers, and at 1.5 to 0.3 densities for the negative films and papers.

Example 1B

Example 1 was repeated with the exception that bromide-free developer was used instead of water in the reconstitution step. The amounts of developer ingredients and bromide-free developer are indicated in Table D. Sensitometric activity was as reported in Table C, above.

TABLE D

Ingredient	Concentration in Spent Developer	Amount Added to 4.4 gal of Spent Developer
Potassium bromide	6.8 gm/Liter	--
Erythorbic Acid	96% of original level (76.8 gm/L)	3.7 g
PMT	67.9% of original level (0.0679 gm/L)	0.032 g
4-hydroxymethyl-4-methyl-1-p-henyl-3-pyrazolidone	91.7% of the original level (0.4585 gm/L)	0.042 g
Benzotriazole	93% of the original level (0.4650 gm/l)	0.035 g
Bromide-free developer		to make 10 gallons

Example 2

The following example demonstrates the improved efficiency of the present process using the preferred developer composition.

A fresh developer composition was made as shown in Table E.

TABLE E

Ingredient	Gram/liter working strength
Tri-sodium ethylene-diaminotetraacetic acid (EDTA)	3.5
Sodium bisulfite	22
Potassium bromide	8
Erythorbic acid	40
4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	0.5
Benzotriazole	0.25
Phenylmercaptotetrazole (PMT)	0.05
Phenylethyl picolium bromide (PPB)	0.3
Water to 1 Liter	

The pH of the solution was adjusted to 10.7 using a 2:1 hydroxide:carbonate buffer solution. The developer solution was placed into the developer tank of a deep tank processor and maintained at 100°F. Various black-and-white graphic arts films were processed and sensitometrically tested, and spent developer collected as in Example 1A.

After 9 gallons of spent developer were collected in the off-line tank, the spent developer was filtered with a 10 micron particle size filter and a sample of the spent developer was analyzed to determine the concentration of potassium bromide, erythorbic acid, Dimezone-S, PMT, benzotriazole, and PPB as in Example 1A. The concentration of PPB was determined using HPLC. Results of the analysis are reported in Table F.

Based upon the bromide concentration, 1 gallon of spent developer was removed from the off-line tank. To the remaining 8 gallons of spent developer, ingredients were added in the amounts indicated in Table F and enough water was added to make 10 gallons and the pH was adjusted to 10.7. The recycled developer was added as a replenishment solution to the developer tank in the processor.

TABLE F

Ingredient	Concentration in Spent Developer	Amount Added to 8 gal of Spent Developer
Potassium bromide	9.38 gm/liter	--
Erythorbic Acid	100% of original level (40 g/l)	301.6 g
PMT	96.9% of original level (0.048 g/l)	0.44 g
4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	100% of the original level (0.5 g/l)	3.77 g
Benzotriazole	100% of the original level (0.25 g/l)	1.88 g
PPB	80.9% of the original level (0.24 g/l)	4.07 g

The cycle of processing, collection, reconstituting and reuse was repeated 10 times and the sensitometric performance of films processed in recycled developer was compared to that of films processed in fresh developer, all as in Example 1A. Results are reported in Table G.

TABLE G

FILM	EXPOSURE	DEVELOPER	[1]RELATIVE SPEED	[2]RELATIVE GRAD	Dmax
CPR (positive camera speed)	Point source 4 ft. candles, 4 sec	FRESH RECYCLED CUFD	100 97.6 95.2	100 104 106	4.3 4.3 4.5
ONF (negative camera speed)	Point source 0.2 ft. candles, 12 sec	FRESH RECYCLED CUFD	100 92.8 98.6	100 98 116	4.9 5.2 5.3
BLD (bright light positive)	Xenon flash 15 sec	FRESH RECYCLED CUFD	100 109.5 95.2	100 95 105	5.6 5.4 5.7
BLF (bright light negative)	Xenon flash 15 sec	FRESH RECYCLED CUFD	100 102.5 102.5	100 94 100	5.3 5.4 5.6
CHC (image-setting film)	*10^{-3} sec, with 5 color correction and 0.7 neutral density filters	FRESH RECYCLED CUFD	100 108.8 90.3	100 96.3 92.6	5.3 5.5 5.8
CHC-P (paper)	*10^{-3} sec, with 5 color correction and 0.7 neutral density filters	FRESH RECYCLED CUFD	100 100 79	100 90.9 100	1.6 1.7 1.8

Claims

1. A process for recycling hydroquinone-free black-and-white photographic developer compositions comprising the steps of:
   a) collecting spent developer; and
   b) reconstituting the developer for re-use.

2. The process of Claim 1, wherein the photographic developer composition comprises a developing agent selected from the group consisting of
   (1) ascorbic acid and sugar-type derivatives thereof,
   (2) stereoisomers and diastereoisomers of ascorbic acid and their sugar-type derivatives,
   (3) salts and mixtures of (1) and (2),
   (4) 2-keto gluconic acid and derivatives thereof, and
   (5) mixtures of (1) through (4).

3. The process of Claim 1, further comprising the step of filtering the spent developer.

4. The process of Claim 1, further comprising the step of analyzing the spent developer.

5. The process of Claim 1, wherein the step of reconstituting the developer comprises the steps of adding fresh ingredients and diluting the developer.

6. The process of Claim 5, wherein the fresh ingredients comprise developing agent, secondary developing agent, and antifogging agent.

7. The process of Claim 6, wherein the antifogging agent is selected from benzotriazole; phenylmercaptotetrazole; and benzimidazole and derivatives thereof.

8. The process of Claim 6, wherein the secondary developing agent is selected from pyrazolidones and derivatives thereof; and metol and derivatives thereof.

9. The process of Claim 1, wherein the photographic developer composition comprises 7 to 10 grams/Liter of an alkali metal bromide.

10. The process of Claim 2, wherein the photographic developer composition further comprises 7 to 10 grams/Liter of an alkali metal bromide.

11. The process of Claim 1, wherein the photographic developer composition comprises

Ingredient	Amount (Grams)
sulfite	3 to 50
sequestering agent	1 to 7
bromide	1.5 to 10.0
developing agent	20 to 90
secondary developing agent	0.25 to 3.0
antifoggants	0.05 to 0.65
development accelerator	0.01 to 3.0
Water	to make 1 Liter

12. The process of Claim 1, wherein the photographic developer composition comprises: Ingredient Amount (Grams)

sulfite ion	15.8
Tri-sodium EDTA	3.5
Potassium bromide	8
Sodium Erythorbate	40
Glucono Delta Lactone	0.7
4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	0.5
Benzotriazole	0.25
Phenylmercaptotetrazole	0.05
PPB	0.3
Water	to make 1 Liter

13. A recycled black-and-white photographic developer composition made according to the process of Claim 1.

14. The recycled developer composition of Claim 13, comprising at least 30% (by volume) of recycled material.

15. The recycled developer composition of Claim 13, comprising 7 to 10 grams/Liter of an alkali metal bromide.

16. The recycled photographic developer composition of Claim 13, comprising

Ingredient	Amount (Grams)
sulfite ion	3 to 50
sequestering agent	to 7
bromide ion	1.5 to 10.0
developing agent	20 to 90
secondary developing agent	0.25 to 3.0
antifoggants	0.05 to 0.65
development accelerator	0.01 to 3.0
Water	to make 1 Liter

17. The recycled photographic developer composition of Claim 13, comprising

Ingredient	Amount (Grams)
sulfite ion	15.8
Tri-sodium EDTA	3.5
Potassium bromide	8
Sodium Erythorbate	40
Glucono Delta Lactone	0.7
4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	0.5
Benzotriazole	0.25
Phenylmercaptotetrazole	0.05
PPB	0.3
Water	to make 1 Liter