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(54) Method for evaporation treatment of photographic processing waste solution and device therefor.

(57) Disclosed is a method for treating a photographic processing waste solution which comprises evaporating a photographic processing waste solution by heating and cooling a vapor generated by the heating by use of a cooling device to obtain a distilled solution, and a treatment device therefor which comprises a treatment tank for performing heating treatment of the photographic processing waste solution, a device for discharging the heated and concentrated solution of the photographic processing waste solution from the treatment tank, a receiving tank for the discharged solution, a device for performing cooling treatment of vapor generated by the heating treatment, a recovering tank for recovering a distilled solution generated by the cooling treatment, and a control device for controlling heating treatment according to the progesss of treatment of the waste solution.

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Method for evaporation treatment of photographic processing waste solution and device therefor

BACKGROUND OF THE INVENTION

This invention relates to a method for evaporation treatment which comprises carrying out evaporation treatment of a waste solution generated with developing processing of a light-sensitive photographic material by means of an automatic processing machine for photography (herein abbreviated as photographic processing waste solution or waste solution) and a device therefor, particularly, to a method for evaporation treatment of a photographic processing waste solution and a device therefor which is suitable for treatment by arrangement within an automatic processing machine or in the vicinity of an automatic processing machine.

Generally speaking, photographic processing of a light-sensitive silver halide photographic material has been performed by a combination of the steps each employing a processing solution having one or two or more functions of developing, fixing, water washing, etc., in the case of a monochromatic light-sensitive material or color developing, bleach-fixing (or bleaching and fixing), water washing, a stabilizing, etc., in the case of a color light sensitive material.

And, in photographic processing which processes a large amount of light-sensitive materials, there has been employed a means to maintain the performance of a processing solution constant by supplementing the components consumed by processing on one hand, while removing the components which are thickened by dissolving out into the processing solution or evaporation by processing (such as bromide ions in a developing solution, silver complexes in a fixing solution) on the other, thereby maintaining constantly the processing solution components. For the above replenishment, a replenisher is supplemented to the processing solution, and a part of the processing solution is discarded for removal of the thickened components in the above photographic processing.

In recent years, the replenisher, including washing water which is the replenisher for water washing, is changing to a system in which the supplemented amount is reduced to a great extent for the reason in pollution or in economy, but the photographic processing waste solution is led from the processing tank of an automatic processing machine through a waste solution pipe and diluted with waste solution of washing water or cooling water of the automatic processing machine, etc., before discarded into sewage, etc.

However, on account of tightened pollutative regulation in recent years, although washing water or cooling water can be discarded into sewage or rivers, it has become substantially impossible to discard other photographic processing solutions other than these [for example, developing solution, fixing solution, color developing solution, bleach-fixing solution (or bleaching solution, fixing solution), stabilizing solution, etc.]. For this reason, the respective photographic processing dealers are asking professional waste solution disposal dealers for recovery of the waste solutions with payment

of recovery fees or providing installations for prevention of environmental pollution. However, comission to waste solution disposal dealers requires a considerable space for storage of waste solutions and is very expensive in cost, and further the installations for prevention of environmental pollution have the drawbacks that initial cost is extremely great, and that a considerably vast space is required for installation. More specifically, as the pollution treatment method which can reduce the pollution load of a photographic processing waste solution, there have been known the active sludge method (e.g. Japanese Patent Publications Nos. 12943/1976 and 7952/1976, etc.), the evaporation method (Japanese Unexamined Patent Publications Nos. 89437/1974 and 33996/1981, etc.), the electrolytic oxidation method (Japanese Unexamined Patent Publications Nos. 84462/1973, 119458/1974, Japanese Patent Publications No. 43478/1978, Japanese Unexamined Patent Publication No. 119457/1974, etc.), the ion exchange method (Japanese Patent Publication No. 37704/1976, Japanese Unexamined Patent Publication No. 383/1978, Japanese Patent Publication No. 43271/1978, etc.), the reverse osmosis method (Japanese Unexamined Patent Publication No. 22463/1975, etc.), the chemical treatment method (Japanese Unexamined Patent Publication No. 64257/1974, Japanese Patent Publication No. 37396/1982, Japanese Unexamined Patent Publications Nos. 12152/1978, 58833/1974, 63763/1978, Japanese Patent Publication No. 37395/1982, etc.), etc., which have not yet proved to be satisfactory.

On the other hand, for the reasons such as restriction in water resources, elevation in water feeding and discharing costs, simplicity in automatic processing machine installation, working environment around automatic processing machine, etc., photographic processing by means of an automatic processing machine

requiring no piping for feeding and discharging of water washing outside of the automatic processing machine by use of stabilizing processing substituting for water washing (the so-called no water washing automatic processing machine) is prevailing in recent years. According to such a processing, it has been desired to omit also the cooling water for temperature control of the processing solution. Such photographic processing using substantially no washing water or cooling water has features that its pollution load is extremely greater as compared with the case when water washing processing is applied, because the photographic processing waste solution from the automatic processing machine is not diluted with water, while on the other hand the waste solution amount is small. Thus, due to the small waste solution amount, the piping outside of the machine for feeding the waste solution can be omitted, whereby an extremely great advantage can be exhibited that compaction and simplification of the machine to the extent available as an office machine can be accomplished, with cancellation of all the drawbacks which have been considered the drawbacks of the automatic processing machine of the prior art, such that the machine can be moved with difficulty after provision of the piping, that the space around foot is narrow, that enormous cost is required for pipeline work during installation, that energy cost is required for feeding hot water, etc.

However, on the other hand, its waste solution has an extremely high pollution load, and therefore it cannot be discarded at all not only into rivers but also into sewage in view of the pollutative regulation. Further, although the amount of waste solution from such a photographic processing (processing performing washing with large amount of water) may be small, even by a relatively small scale processing, its amount can be

about 10 liters per day in processing of, for example, X-ray light-sensitive materials, about 30 liters per day in processing of light-sensitive materials for printing plates, and about 50 liters per day in processing of color light-sensitive materials. Thus, processing of the waste solution is becoming an increasingly great problem in recent years.

For the purpose of carrying out easily processing of a photographic processing waste solution, a device for evaporating water to dryness by heating a photographic processing waste solution is disclosed in Japanese Unexamined Utility Model Publication No. 70841/1985. Even in such a device, since a vapor generated by subjecting the photographic processing waste solution to evaporation concentration or drying is discharged into atmosphere, is poses a problem in view of prevention of environmental pollution and a problem of worsened working environment due to generation of objectionable odor. Also, as an embodiment, the device is provided with a means having an activated charcoal for adsorbing and removing injurious substances in vapor. However, the adsorption of injurious substances is not sifficiently performed only by use of the activated charcoal, and the activated charcoal has a problem of absorption of vapor. Therefore, an exchanging frequency of the activated charcoal is large and the cost concerning them is raised. Moreover, since this device discharges hot vapor into atmosphere, it requires a means for discharging vapor to outside of room when this device is employed in room. Also, this device treats the photographic processing waste solution to dryness, and therefore had the drawbacks such that a part of the photographic processing waste solution components was converted to a tar which was attached on a heating source or an evaporation kettle wall to cause lowering in heat efficiency, that due to the presence of a surfactant added into the photographic

processing solution or dissolved out and accumulated from the light-sensitive material, foaming may sometimes occur to cause bumping, that objectionable odor is conspicuous and excessive decomposition may sometimes occur, and that breaking of the evaporation kettle may sometimes occur, etc.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 and 10 is a schematic illustration showing an evaporation treatment device for a photographic processing waste solution of the present invention;

Fig. 2 is a flow chart showing another example of the present invention;

Fig. 3 through Fig. 9 are each schematic illustration showing the cooling treatment means of the present invention.

SUMMARY OF THE INVENTION

The pricipal object of the present invention is to further develop the thought of the evaporation treatment device for photographic processing waste solution as disclosed in Japanese Unexamined Utility Model Publication No. 70841/1985 and at the same time clarify various improvements for practical application of the device, particularly to clarify a treatment method and an evaporation and cooling treatment device of a photographic processing waste solution which is optimum for treatment of a photographic processing waste solution in a photographic processing installation where a single or a small number of automatic processing machines are arranged. Further, another object is to provide a treatment method and an evaporation and cooling treatment device of a photographic processing waste solution which is free from the drawbacks or inconveniences, etc., as

mentioned above and can process easily the vapor generated by treatment of a photographic processing waste solution to obtain distilled solution.

The method for treatment of a photographic processing waste solution according to the present invention accomplishing the above objects is a method which comprises evaporating a photographic processing waste solution by heating and cooling a vapor generated by the heating by use of a cooling means to obtain a distilled solution.

More preferably, the method of the present invention further comprises absorbing a conentrate of the photographic processing waste solution concentrated by heating onto a carrier to perform solidification treatment.

The evaporation and cooling treatment device of the photographic processing waste solution according to the present invention accomplishing the above objects comprises a heating means for heating photographic processing waste solution and a cooling treatment means for cooling vapor generated by said heating means, the device has a constitution in which said cooling treatment means receives the vapor directly or indirectly from said heating means.

In the present specification, distilled solution means a distilled liquid, including the case containing components other than water.

A preferable embodiment of the method of the present invention comprises (1) performing at least one cooling treatment selected from (A) to (G) shown below, that is (A) the treatment by means of a baffle or a radiating plate, (B) the treatment in which the waste water before evaporation concentration or drying treatment is used as the cooling heat medium, (C) the treatment which is carried out in a tank which stocks the waste solution, (D) the above treatment (C) in which

there are a plural number of stock tanks, (E) the treatment in which the waste solution before evaporation concentration or drying treatment is introduced into the cooling treatment section to be utilized for cooling, (F) the treatment in which a fan for air cooling is utilized, (G) the treatment which is carried out through heat exchange with the processing tank, the replenisher tank or the dissolving water tank of the automatic processing machine; (2) the photographic processing waste solution containing a waste solution of the stabilizing solution substituting for water washing; or (3) gas adsorption treatment being performed before cooling treatment.

Preferable embodiments of the solidification treatment of the concentrate according to the present invention is (A) wherein the solidification treatment is a liquid absorbing treatment onto a liquid absorbable resin, (B) wherein the solidification treatment is the treatment with addition of a solidifying agent or a drying agent, (C) wherein the solidification treatment is carried out by use of a pack for waste solution housing at least one of the absorbable resin, the solidifying agent and the drying agent, the concentrated soluiton of the photographic processing waste solution being solidified by absorption into said pack and the solid being housed into said pack, or (D) wherein the solidification treatment is carried out by throwing at least one of the liquid absorbable resin, the solidifying agent and the drying agent into an evaporation concentration kettle.

Alternatively, according to the most preferred embodiment of the method of the present invention, a photographic processing waste solution overflowed from the photographic processing tank of an automatic processing machine is stored in a stock tank, and following the photographic processing waste solution information obtained by detecting its amount and/or the

photographic processing waste solution amount in the treatment means, the photographic processing waste solution is fed from the stock tank to the treatment means, wherein it is evaporated by a heating means to evaporate the photographic processing waste solution, and its vapor is cooled to distilled solution according to the energy-saving and efficient heat exchange method.

On the other hand, the treatment device of the photographic processing waste solution according to the present invention accomplishing the above objects comprises a treatment tank for performing heating treatment of a photographic processing waste solution, a means for discharging from said treatment tank the heated and concentrated solution of the photographic processing waste solution, a receiving tank for receiving the discharged solution, a means for performing cooling treatment of vapor generated by said heating treatment, a recovering tank for recovering a distilled solution generated by said cooling treatment, and a control means for controlling heating treatment according to the progress of treatment of the waste solution.

Still another preferable embodiment of the evaporation treatment device according to the present invention is one wherein the solidification treatment means is a waste solution pack housing at least one of a liquid absorbable resin, a solidifying agent and a drying agent for one treatment, having a constitution such that said waste solution pack is thrown into the concentrate of the photographic processing waste solution or that the concentrate of the photographic processing waste solution is introduced into said waste solution pack.

Alternatively, according to the most preferred embodiment of the evaporation treatment device of the present invention, the photographic processing waste solution is stored in a stock tank, and following the photographic processing waste solution information

obtained by detecting its amount and/or the photographic processing waste solution amount in the treatment means, the photographic processing waste solution is fed from the stock tank into (evaporating concentration) treating means, wherein the photographic processing waste solution is concentrated by evaporation with a heating means, and the concentrate is solidified within said treatment means or by flowing out of said means, simultaneously with cooling of the vapor to distilled solution to be reutilized in the photographic processing steps.

In the present invention, it is preferred to recover silver according to a means such as the electrolytic method, the precipitation method, the metal substitution method, the reduction method, etc., before heating treatment.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, the present invention will be described in detail.

First, the cooling treatment means 60 in the present invention shown in Fig. 1 is described.

For cooling of the vapor generated by evaporation of a photographic processing waste solution, all kinds of heat exchange means can be employed, including any of the constitutions shown below:

(1) the shell and tube type (multi-tubular type, muffled tube type);
(2) the double tubular type;
(3) the coil type;
(4) the helical type;
(5) the plate type;
(6) the fin tube type;
(7) the trombone type; and
(8) the air cooling type.

The heat exchange type reboiler technique can be

also used, for example:

(1) the vertical thermosiphon type;

(2) the horizontal thermosiphon type;

(3) the overflow tubular type (the kettle type);

(4) the forced circulation type;

(5) the insertion type, etc.

Further, the condenser type heat exchange technique may be employed, and any of the following systems may be employed:

(1) the direct condenser system;

(2) the tower built-in system;

(3) the tower top setting system;

(4) the separation system, etc.

It is also possible to use a cooler, and any desired type of cooler may be used.

It is also advantageous to employ an air cooling system heat exchanger and either one of

(1) the forced drafting system and

(2) the blowing drafing system may be employed.

In the following, preferable examples of the cooling treatment means 60 are described.

(1) As shown in Fig. 3, a constitution wherein the vapor Q generated by evaporation treatment of the photographic processing waste solution P is passed through a radiation plate device 62 having a large number of fins 61 for air cooling.

(2) As shown in Fig. 4, a constitution wherein the vapor Q generated by evaporation treatment of the photographic processing waste solution P is passed through the cooling section 66 such as a coil 63, etc., where heat exchange is effected with the photographic processing waste solution P in the stock tank 30.

(3) As shown in Fig. 5, a constitution wherein the vapor Q generated by evaporation treatment of the photographic processing waste solution P is passed through the cooling section 66 such as a multi-stage coil

64, etc., where heat exchange is effected with photographic processing waste solution P in a plural number of stock tanks 30 and 31.

(4) As shown in Fig. 6, a constitution wherein the vapor Q generated by evaporation treatment of the photographic processing waste solution P is passed through the cooling section 66 such as a coil 63 (or 64) which sprays the photographic processing waste solution P from a spraying member 65.

(5) As shown in Fig. 7, a constitution wherein the vapor Q generated by evaporation treatment of the photographic processing waste solution P is passed through the cooling section 66 such as a coil 63 (or 64), etc., against which wind is blown by means of an air delivering means 67 such as a fan, etc.

(6) As shown in Fig. 8, a constitution wherein the vapor Q generated by evaporation treatment of the photographic processing waste solution P is passed through the cooling section 66 such as a coil 63, etc., where heat exchange is effected with the photographic processing solution used in at least one tank of the color developing tank SD, the bleach-fixing tank BF, the stabilizing tank substituting for water washing Sb or at least one solution in the replenisher tank S.

(7) As shown in Fig. 9, a constitution wherein the vapor Q generated by evaporation treatment of the photographic processing waste solution P is passed through a heat exchanger 69 having heat exchange particles 68 comprising a large number of glass beads, etc., built therein.

(8) Otherwise, as to the cooling means by use of a baffle, for example, a constitution wherein the vapor Q generated by evaporation treatment of the photographic processing waste solution P is passed between the baffles as disclosed in Japanese Unexamined Patent Publication No. 125600/1978.

In the present invention, it is preferable to use one of a combination of two or more of the heat exchange cooling treatment means of these (1) to (8) and others.

When the gas adsorption treatment to be used in the present invention is desulfurization treatment, said desulfurization treatment may be either dry system desulfurization or wet system desulfurization. As the former dry system desulfurization, there can be used various desulfurization methods such as the iron oxide method or the soda-iron method and contact adsorption by use of activated charcoal, silica gel, molecular sieve, etc., or the oxidation desulfurization method, etc. On the other hand, as the wet system desulfurization method of the latter case, either non-regeneration method or regeneration method may be employed. For example, there may be employed any of the method in which sulfur is absorbed into an alkaline solution, the method in which reducing property of hydrogen sulfide is utilized or the mehtod in which a compound of hydrogen sulfide is formed, etc., and, as to the operational method, either one of the methods such as the seaboard method, the cyclox method, the vacuum carbonate method and the garbottle method, etc.

The gas adsorption treatment to be used in the present invention is not limited to the above desulfurization treatment, but the zeolite adsorption treatment, the activated charcoal treatment, etc., may be also practiced for the purpose of removing ammonia gas or sulfur gas.

In the present invention, the preferable embodiment of the gas adsorption treatment further comprises a means for reutilizing distilled solution R including a gas adsorption means 50 such as a filer, an adsorbent and a cooling means for vapor 60.

In the drawings, the gas adsorption means 50 separates and recovers injurious gas such as hydrogen

sulfide, oxygen sulfide or ammonia gas (H_2O, SO_2, NH_3, etc.) contained in the vapor of the photographic processing waste solution by use of various desulfurization and adsorption techniques utilizing, for example, zeolite adsobent, activated charcoal as mentioned above.

According to a preferred embodiment of the present invention, (1) at least one secondary treatment selected from the following (A) to (I) is carried out to the distilled solution, namely (A) activated charcoal treatment, (B) UV-ray irradition treatment, (C) reverse osmosis treatment, (D) oxidation agent treatment, (E) electrolytic oxidation treatment, (F) aeration treatment, (G) electrodialysis treatment, (H) redistillation treatment, (I) ion exchange resin treatment is carried out; (2) the distilled solution is used as the dissolving water for photographic processing solution; (3) gas adsorption treatment is conducted together with distillation, preferably one or two or more of desulfurization treatment, zeolite adsorption treatment, activated charcoal treatment is conducted in combination.

Also, according to the most preferred embodiment of the present invention, the photographic processing waste solution overflowed from the photographic processing tank of an automatic processing machine is stored in a stock tank, and following the photographic processing waste solution information obtained by detecting its amount and/or the amount of the photographic processing waste solution in the treatment means, the photographic processing waste solution is fed from the stock tank to the treatment means, where the photographic processing waste solution is evaporated by a heating means to be concentrated or dried, and the resulting vapor is cooled and reutilized as distilled solution in the photographic processing steps.

The activated charcoal to be used in the present

invention may be any activated charcoal having adsorbing capacity for at least one materials of benzyl alcohol, ammonium compounds and sulfur compounds.

In the present invention, regardless of the starting material and the method for activation, either powdery or granular activated charcoal can be used, preferably granular activated charcoal, particularly preferably coconut shell activated charcoal and activated charcoal having molecular sieve ability. The activated charcoal having molecular sieve ability as herein mentioned has slit-like fine pores, and the size of the fine pores should desirably be 6 Å or more, with the width being 15 Å or less. As to the activated charcoal having such molecular sieving ability, reference can be made to the description in Japanese Unexamined Patent Publication No. 14831/1983.

As the adsorbable substance to be used in the adsorption treatment, etc., in the present invention, the following substances other than activated charcoal can be also used.

(1) Clay substance
(2) Polyamide type polymeric compound
(3) Polyurethane type polymeric compound
(4) Phenol resin
(5) Epoxy resin
(6) Polymeric compound having hydrazide group
(7) Polymeric compound containing polytetrafluoro-ethylene
(8) Monovalent or polyvalent alcohol methacrylic acid monoester-polyvalent alcohol methacrylic acid
(9) Polyester copolymer

As to details about these substances (1) to (9), reference can be made to the description in Japanese Unexamined Patent Publication No. 124639/1984 (particularly pages 62 to 66).

The UV-ray to be used in the present invention can

be generally obtained by a commercially available UV-ray lamp or UV-ray irradiation device or a halogen lamp, etc., and is not particularly limited. The output of the UV-ray lamp, etc., has been known to be 5 W to 1 KW, but it is not limited thereto. Also, in the present invention, electromagnetic wave and light with wavelength outside the range of 190 nm to 400 nm is generated from the UV-ray lamp, and it may be irradiated on the distilled solution obtained from the photographic processing waste solution. Also, Infrared-ray, etc., may be used in combination.

The UV-ray lamp, etc., to be used in the present invention can be also made a double tube.

In the present invention, by UV-ray irradiation is meant UV-ray irradiation of the distilled solution obtained from a photographic processing waste solution by use of a UV-ray lamp, etc., and these UV-ray irradiations may be effected on said distilled solution continuously or, if desired, intermittently.

In the reverse osmosis treatment to be used in the present invention, various kinds of reverse osmosis membranes, desalting concentration methods and devices by use of reverse osmosis membranes can be utilzed without any limitation.

The reverse osmosis device should preferably be run under a pressure of 40 kg/cm^2 to 55 kg/cm^2 with respect to separation performance and treatment capacity.

The oxidizing agent to be used in the oxidizing agent treatment of the present invention is inclusive of metal, non-metal oxides, oxyacids and salts thereof, peroxides, organic oxygen containing compounds, etc. Examples of oxides may include nitrogen peroxide NOx, anhydrous chromic acid CrO_3, selenium dioxide SeO_2, manganese dioxide MnO_2, lead dioxide PbO_2, osmium tetraoxide OsO_4, silver oxide Ag_2O, copper oxide CuO, mercury oxide HgO, etc. Oxyacids may be exemplified by

hot sulfuric acid H_2SO_4, nitrous acid HNO_2, nitric acid HNO_3, etc. As the salt, there may be employed sodium hypochlorite NaOCl, bleaching powder $CaOCl_2$, potassium bichromate $K_2Cr_2O_7$, potassium chromate $K_2Cr_2O_4$, potassium permanganate $KMnO_4$, potassium chlorate $KClO_3$, potassium perchlorate $KClO_4$, etc. Typical examples of peroxides are hydrogen peroxide H_2O_2, sodium peroxide Na_2O_2, benzoyl peroxide $(C_6H_5COO)_2$, etc. There may be also included substances which can take 2 or more kinds of valences, such as trivalent iron ion Fe^{3+}, divalent copper ion Cu^{2+}, lead tetraacetate $Pb(CH_3Co_2)_4$, etc. Otherwise, Fentone reagent ($Fe^{++} + H_2O_2$), dehydrogenation catalysts (Pt, Se, Zn), etc., can be also used as the oxidizing agent.

The electrolytic oxidation treatment to be used in the present invention is a method for oxidizing a substance on the anode by electrolysis, and it may be any system by way of increase of positive charges of cations, decrease of negative charges of anions, polymerization of anions, increase of oxygen atoms and decrease of hydrogen atoms in atomic groups. The excellent point of such electrolytic oxidation as compared with oxidation with an oxidizing agent is that very strong oxidation can be effected and also that there is little by-product.

The aeration treatment in the present invention is to promote oxidation by air delivery into the distilled solution of the photographic processing waste solution, and it is preferable to make finer the air bubbles by use of a distributor, etc., whereby the bubbling effect can be improved to enhance removal efficiency of organic solvents, etc.

The electrodialysis treatment of the present invention is to charge the distilled solution of the photographic processing waste solution into the chambers each partitioned by a diaphragm between the cathode and the anode of an electrodialytic cell and pass direct

current therethrough.

Preferably, the diaphragms are ion exchange membranes. More preferably, the space between the cathode and the anode should be partitioned with anion exchange membranes and cation exchange membranes to provide a cathode chamber, a plural number of concentration chambers (the chamber partitioned with an anion exchange membrane on the cathode side and a cation exchange membrane on the anode side), a plural number desalting chambers (the chamber partitioned with a cation exchange membrane on the cathode side and with an anion exchange membrane on the anode side) and an anode chamber. The distilled solution of the photographic processing waste solution is preferably charged into the desalting chambers, but it is also preferable to charge it into the concentration chamber. The electrolyte solution to be charged into the concentration chambers and the anode chamber is not particularly limited, but 0.1 to 2 N solutions of, for example, sodium sulfite, sodium sulfate, sodium chloride, potassium sulfate, sodium thiosulfate, etc., can be preferably used. In this case, a processing solution having fixing ability (bleach-fixing solution or fixing solution) or its waste solution can be very preferably used as the electrolyte solution to be charged into the concentration chambers and the anode chamber, because no electrolyte solution is particularly required.

The redistillation treatment to be used in the present invention is to carry out distillation treatment of the concentrate obtained from the photographic processing waste solution, which is one of the so-called rectifying operation. It may be either batchwise distillation (including simple distillation, batchwise rectification) or continuous distillation, and it is also possible to employ the continuous equilibration distillation method for continuous rectification. To

obtain pure water (containing remarkably little distillate other than water) by the redistillation treatment will make it possible to feed effectively water to the photographic processing solutions. Also, an appropriate separating agent may be advantageously used in azeotropic distillation and extraction distillation. In the present invention, the secondary treatment effect can be obtained also by the so-called steam distillation. Also, as for the operational pressure, it may be either of high pressure distillation, normal pressure distillation, vacuum distillation and molecular distillation.

The ion exchange resin treatment in the present invention can be carried out by the contact betweent various kinds of ion exchange resins and the photographic processing waste solution, and the ion exchange resins may comprise three-dimensionally polycondensed polymer substrates having functional groups bonded thereto, including cation exchange resin, anion exchange resin, chelating resin, absorptive resin, etc.

As to the chemical structure examples of the ion exchange resins preferably used in the present invention and the methods for using them, reference can be made to the description in Japanese Unexamined Patent Publication No. 124639/1984 (particularly pages 54-57).

The carrier to be used in the present invention is capable of absorbing the concentrate of the photographic processing waste solution, preferably one which is free from liquid dripping even when the liquid absorbable carrier having absorbed a liquid is held by hands, and the so-called high liquid absorbable resin is preferably used.

As the high liquid absorbable resin, there may be used, for example, seed polysaccharides, algae polysaccharides, resin polysaccharides, fruits saccharides and route stock polysaccharides. There may

be further included zansane gum, zanflow, guardrane, succinoglucane, sizophirane, pullulan, gelatine, casein, albumin, shellac, starch derivatives, derivatives of guar gum, locust bean gum, and cellulose derivatives, alginic acid derivatives, vinyl type compound, acrylic compound, polyethylene oxide, etc.

Next, preferable examples of the high liquid absorbable resin to be used in the present invention are shown below.

(A) Grafted starch type

(A-1) Starch-acrylonitrile grafted polymer

(A-2) Starch-acrylic acid grafted polymer

The above (A-1) can be prepared according to the methods disclosed in Japanese Unexamined Patent Publication No. 43395/1974 and U.S. Patent No. 4,134,863, and the above (A-2) can be prepared according to the method disclosed in Japanese Patent Publication No. 46199/1978. (B) Acrylic acid type:

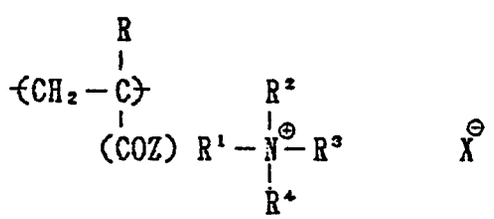
(B-1) Sodium polyacrylate type

(B-2) Vinyl alcohol-acrylic acid copolymer type

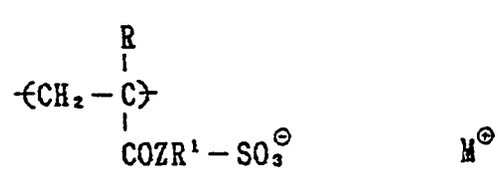
The above (B-2) can be also used repeatedly by natural drying and/or forced drying.

(C) Polymers having recurring units having the structural formula represented by (I) or (II) shown below, more preferably having 10 to 70 % by weight of (I) and/or (II) copolymerized with another ethylenic unsaturated monomer

(I)



(II)



In the above formulae, R is a hydrogen atom, a methyl group or a halogen atom; Z is an oxy group or an imino group; n is 0 or 1; R^1 is an alkylene group having 1 to 6 carbon atoms (including also substituted alkylene groups), a cycloalkylene group having 5 to 6 carbon atoms or an arylene group, and arylenealkylene group or an arylenebisalkylene group, wherein said alkylene moiety has 1 to 6 carbon atoms and said arylene moiety (which may be also substituted) has 6 to 10 carbon atoms, and includes an arylene substituted with a hydrophilic polar group such as $-NHCR^5$ (O), $-OH$, $-C\equiv N$, $-C(=O)NR^5$, or $-C(=O)-O-M^{\oplus}$ (wherein R^5 is an alkyl group having 1 to 4 carbon atoms); R^2, R^3 and R^4 are each hydrogen atom or an alkyl group having 1 to 6 carbon atoms, or forms together with N a heterocyclic group which can also contain optionally sulfur or oxygen atom; M is a hydrogen atom, a soluble cation or an ammonium group including quaternary ammonium cations having alkyl groups having not more than 6 carbon atoms; and X is an acid anion.

The halogen substituent on R can be bromine or chlorine, the alkylene group having 1 to 6 carbon atoms of R^1 may be also substituted with hydroxyl group, the arylenealkylene group of R^1 includes phenylenemethylene group, phenyleneethylene group, phenylenepropylene group and phenylenebutylene group, and the arylenebisalkyl group of R^1 includes phenylenedimethylene group.

Examples of the soluble cation of M are sodium and potassium.

Examples of the heterocyclic group formed by R^2, R^3 and R^4, and the N atom to which these are bonded may include pyridinium, imidazolium, oxazolium, thiazolium and morpholium.

The acid anion of X may include chloride, bromide, acetate, p-toluene sulfonate, methane sulfonate, ethane

sulfonate, methylsulfate, ethylsulfate and perchlorate.

The ethylenic unsaturated monomer to be copolymerized with the monomer of the above formula (I) and/or the monomer of the above formula (II) comprises preferably one or more monomer having a crosslinkable group such as 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, and a monomer containing active methylene group. The copolymerizable ethylenic unsaturated monomer polymerized of this type is disclosed in, for example, U.S. Patents Nos. 3,459,790, 3,488,708, 3,554,987, 3,658,878, 3,929,482 and 3,939,130.

The preferable polymer to be used in the above description has 10 to 70 % by weight of recurring units derived from at least one monomer enumerated below:

2-aminoethyl methacrylate hydrochloride;

N-(2-methacryloyloxyethyl)-N,N,N-trimethylammonium chloride;

N-(2-methacryloyloxyethyl)-N,N,N-trimethylammonium methosulfate;

Sodium 2-methacryloyloxyethyl-1-sulfonate; and

2-(N,N-dimethylamino)ethylmethacrylate hydrochloride.

The acid addition salt coinciding with the above structural formula (I) can be converted to a free amine when neutralized with a base.

The above polymer can be prepared according to a conventional method by carrying out polymerization reaction of a suitable monomer in an aqueous solution.

The monomer of the above structural formula (I) can be prepared according to the methods described in "functional monomers" edited by R.H. Yocum and E.B. Nyquist, Marcel Dekker, Inc., New York (1974) and U.S. Patent No. 2,780,604. The monomer of the above structural formula (II) can be prepared according to the methods described in U.S. Patents Nos. 3,024,221 and 3,506,707.

In some cases, the polymer can be prepared by (a) quaternarizing a polymer having amine groups with an alkylating agent, or alternatively (b) by reacting an amine with a polymer having a group reactive with the amine, for example, an active halogenic group. Such techniques are known in this field of art and described in U.S. Patents No. 3,488,706 and 3,709,690 and Canadian Patent No. 601,958.

The resins as mentioned above are also available as commercial products. Examples of such commercial products may include Sumikagel N-100, Sumikagel SP-520, Sumikagel S-50, Sumikagel NP-1020, Sumikagel F-03, Sumikagel F-51, Sumikagel F-75, Sumikagel R-30 (all are trade names, produced by Sumitomo Kagaku Kogyo Co.), Sunwet IM-300, Sunwet IM-1000 (all are trade names, produced by Sanyo Kasei Co.), Aquakeep IOSH-P (trade name, produced by Seitetsu Kagaku Co.), Ranjiel F (trade name, produced by Nippon Exran Co.), etc.

The high liquid absorbable resin preferably used in the present invention should preferably have a shape which can easily absorb liquid, and those shaped in powder or granules with diameters of about 0.01 to 3 mm can be advantageously used in handling.

The solidifying agent to be used in the present invention may be any one capable of solidifying the concentrate of the photographic processing waste solution, and the chemical reaction may be either accompanied or not during solidification. As the solidifying agent of the present invention, for example, CaO, $Ca(OH)_2$, $CaCO_3$, silica gel, calcium chloride, aluminum oxide, calcium sulfate, magnesium oxide, barium oxide, granulate soda lime, diphosphorous pentaoxide, etc.

In the present invention, it is preferred that the processing chamber 42 in Fig. 1 should be constituted so as to store the photographic processing waste solution to

be treated or the concentrate which has been already treated, an inner kettle or inner liner 44 formed of a metal or a porcelain or a synthetic resin, etc., and the treated concentrate solidified according to the present invention as shown below in Examples, by use of a separating means such as bag filter or pack, etc., and taken out together with the inner kettle or inner liner 44 or together with the bag filter or the pack to be discarded or disposed. Other than utilizing the above mentioned inner kettle or inner liner 44, the discharging means 43 can be designed variously. For example, the concentrate of the photographic processing waste solution is permitted to fall naturally into a vessel containing one or two or more liquid absorbable resin, solidifying agent and drying agent of the present invention through the valve from the bottom of a known discharging device utilizing rotary screw pump or the treatment chamber 42 to effect solidification according to the present invention therein.

The inner liner 44 for pack may be preferably made of a heat-resistant and chemical resistant material, such as carbon fiber, aramide fiber, Teflon resin fiber, hemp, glass fiber, polyethylene foam, polypropylene foam, etc.

Next, typical examples of the photographic processing waste solutions which can be treated according to the present invention are described in detail. In the following description, photographic processing solutions in the case of photographic materials for color to be processed are primarily described, but the photographic processing waste solutions are mostly overflowed solutions discharged during processing of silver halide color photographic materials by use of these photographic processing solutions.

The color developing solution is a processing solution to be used in the color developing processing step (which is the step for formation of a color image,

the step for forming a color image through the coupling reaction of the oxidized product of a color developing agent with a color coupler), and therefore a color developing agent is required to be contained generally in the color developing solution in the color developing processing step, but the case of having a color developing agent built in the color photographic material and processing it with a color developing solution or alkali solution (activator solution) containing a color developing agent is also included. The color developing agent contained in the color developing solution is an aromatic primary amine color developing agent, including amino phenol type and p-phenylenediamine type derivatives.

Examples of the above aminophenol type developing agent may include o-aminophenol, p-aminophenol, 5-amino-2-oxy-toluene, 2-amino-3-oxy-toluene, 2-oxy-3-amino-1,4-dimethyl-benzene.

The color developing solution may sometimes contain an alkali agent conventionally used in a developing solution, and further sometimes contain various additives such as benzyl alcohol, alkali metal halides or development controllers, preservatives. Further, various kinds of defoaming agents or surfactants, or organic solvents such as methanol, dimethylformamide or dimethyl sulfoxide may be sometimes conveniently contained.

Also, antioxidants may be contained in the color developing solution, if desired. Further, in the color developing solution, various chelating agents may be used as the sequestering agent in combination.

The bleach-fixing solution is a processing solution to be used in the bleach-fixing step (which is the step in which the metal silver formed by development is oxidized to be converted to silver halide, and then water-soluble complex is formed simultaneously with color

formation of the uncolored portion of the color forming agent), and the kind of the bleaching agent used in the bleach-fixing solution is not particularly limited.

The bleach-fixing solution may sometimes contain various pH buffering agents either singly or as a combination of two or more kinds. Further, various kinds of fluorescent brighteners, defoaming agents or surfactants may be contained. Also, preservatives such as bisulfite adducts, etc., organic chelating agents such as aminopolycarboxylic acids, etc., stabilizers such as nitro alcohol, nitrates, etc., or organic solvents, etc., may be sometimes conveniently contained. Further, the bleach-fixing solution may sometimes contain various bleaching promotors as disclosed in Japanese Unexamined Patent Publication No. 280/1971, Japanese Patent Publications Nos. 8506/1970 and 556/1971, Belgian Patent No. 770,910, Japanese Patent Publications Nos. 8836/1970 and 9854/1978, Japanese Unexamined Patent Publications Nos. 71634/1979 and, 42349/1974 added therein.

The stabilizing processing by use of a stabilizing solution substituting for water washing according to the present invention is not the conventional processing in which a large amount of water is employed for washing and removing a processing solution of the pre-step adhered to or permeated in the light-sensitive photographic material. This is a processing carried out by replenishing the stabilizing solution in an amount of as small as 30 ml/m^2 to 9,000 ml/m^2, preferably 60 ml/m^2 to 3,000 ml/m^2 to the light-sentsitive photographic material into the stabilizing tank to secure the effects similar as or more than the above conventional processing, and is specifically disclosed as an image stabilizing processing in Japanese Unexamined Patent Publication No. 134636/1983, etc.

Accordingly, by use of the stabilizjing solution substituting for water washing according to the present

invention, there is no requirement to provide pipelines for supplying from and discharging to the outside of the automatic processing machine for water washing as in the concventional process.

The evaporation treatment of the present invention is preferably employed in conmbination with the processing by use of the stabilizing solution substituting for water washing, because an amount of processed waste solution is small and hence a large effect of heat exchange is obtained.

There may be a kind of stabilizing solution which has a function for stabilizing the color image and a function of draining bath for preventing the contamination such as uneven washing. The stabilizing solution may further contain coloring controlling solution and antistatic solution containing antistatic agent. When bleach-fixing components are brought from the pre-bath into the stabilizing solution, there may be provided any provisions to the stabilizing solution for neutralizing, desalting and inactivating the components to prevent a deterioration of dye.

As the component contained in such a stabilizing solution, there may be included chelating agents having a chelate stability constant with iron ions of 6 or higher (particularly preferably 8 or higher). Such chelating agents may include organic carbonic acid chelating agents, organic phosphoric acid chelating agents, polyhydroxy compounds, inorganic phosphoric acid chelating agents, etc. Particularly preferably for the effect of the present invention, diethylenetriaminepenta-acetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid or salts thereof may be employed. These compounds may be used generally at concentrations of about 0.1 g to 10 g per liter of the stabilizing solution, more preferably at concentrations of about 0.5 g to 5 g per liter of the stabilizing solution.

As the compound to be added in the stabilizing solution, ammonium compound may be employed, these are supplied from ammonium salts of various inorganic compounds. As the ammonium compounds, there may be specifically included ammonium hydroxide, ammonium bromide, ammonium carbonate, ammonium chloride, ammonium hypophosphite, ammonium phosphate, ammonium phosphite, ammonium fluoride, ammonium acidic fluoride, ammonium fluoroborate, ammonium arsenate, ammonium hydrogen carbonate, ammonium hydrogen fluoride, ammonium hydrogen sulfate, ammonium sulfate, ammonium iodide, ammonium nitrate, ammonium pentaborate, ammonium acetate, ammonium azide, ammonium lauryltricarbonate, ammonium benzoate, ammonium carbamate, ammonium citrate, ammonium diethyldithiocarbamate, ammonium formate, ammonium hydrogen malate, ammonium hydrogen oxalate, ammonium hydrogen futarate, ammonium hydrogen tartarate, ammonium lactate, ammonium malate, ammonium maleate, ammonium oxalate, ammonium futarate, ammonium picrate, ammonium pyrolidine dithiocarbamate, ammonium salicylate, ammonium succinate, ammonium sulfanate, ammonium tartarate, ammonium thioglycolate, 2,4,6-trinitrophenol ammonium, etc. Amount of the ammounium compound added may be within the range of from 0.05 to 100 g, preferably from 0.1 to 20 g per liter of the stabilizing solution.

As the compound to be added in the stabilizing solution, there may be included pH controllers, antifungal agents as disclosed in Japanese Unexamined Patent Publication No. 43741/1986 pages 26 to 30, such as 5-chloro-2-methyl-4-isothiazoline-3-one, 2-octyl-4-isothiazoline-3-one, 1,2-benzisothiazoline-3-one and others, preservatives such as water-soluble metal salts, etc., dispersing agents such as ethylene glycol, polyethylene glycol, polyvinyl pyrrolidone (PVP K-15, Luviscol K-17, etc.), etc., film hardening agents such as formalin, etc., fluorescent brighteners and so on.

Above all, in the present invention, a stabilizing solution substituting for water washing containing an antifungal agent as mentioned above may be particularly preferably used, because generation of tar in the evaporation treatment device is little.

When the light-sensitive material to be processed is for negative, an aldehyde derivative may be sometimes added in said stabilizing solution for negative for improvement of storability of the photographic image.

In the above stabilizing solution for negative, there may be sometimes added various additives, if necessary, including, for example, water droplet irregularity preventives, pH controllers, film hardeners, orgnaic solvents, humectants, otherwise additives for improving and expanding the processing effects such as tone modifiers, etc.

Also, a stilbene type fluorescent brightener may be sometimes used in a color developing solution or stabilizng solution for color paper.

The components contained in the waste solution of the above color developing solution are various components or additives as described above and the components dissolved out and accumulated from the photographic material to be processed.

The components contained in the waste solutions of the above bleach-fixing solution and the stabilizing solution are various components or additives as described above and the components dissolved out and accumulated from the photographic material, etc.

Next, referring to the drawings, described is an example of the evaporation treatment device of the photographic processing waste solution which is the most preferred embodiment in practicing the present invention.

A).... Automatic processing machine

The automatic processing machine for which the present invention is applied is indicated by the symbol

10 in Fig. 1, and the machine shown in the Figure is of a system in which a roll-shaped light-sensitive photographic material F is guided continuously into a color developing tank CD, a bleach-fixing tank BF and a stabilizing tank substituting for water washing Sb to be photographically processed therein, and after drying D, wound up (although not shown in the drawing, the automatic processing machine is inclusive of various kinds such as the embodiment having a color developing tank CD for permitting a short leader to guide the light-sensitive photographic material, a bleaching tank BL, a fixing tank FIX, a stabilizing tank substituting for water washing Sb and a second stabilizing tank, but a typical example is shown in the Figure).

11 is a replenisher tank, and the replenisher is replenished to the respective processing tanks according to the control device 20 by detecting the photographic processing amount of the light-sensitive photographic material F with a sensor 21 as described in detail below and following the detected information.

The system of photographic processing, the constitution of the photographic processing tanks, the replenishing method of the replenisher are not limited to those as described above, but the present invention is applicable for other systems and constitutions, including the so-called no water washing system as disclosed in Japanese Unexamined Patent Publications Nos. 14834/1983, 34448/1983, 132146/1982, 18631/1983, 263941/1985 and 2153/1986.

Incidentally, though the most preferred embodiment of the present invention is that equipped in the automatic processing machine, when a large amount of the photographic processing waste solution is processed collectively, the processing is preferably carried out by use of the treatment device of the photographic processing waste solution as shown in Figure 10.

Regarding to the device of Figure 10 is essentially the same as the automatic processing machine in the present specification and hence described simulataneously hereinunder.

B).... Recovery of photographic processing waste solution and silver recovery

When the replenisher is replenished to the respective processing tanks, overflowed waste solutions are discharged from the processing tanks and collected in the stock tank 30. During this operation, the waste solution in the color developing tank CD is charged into the stock tank 30 without passing through a silver recovery means 80 according to the silver recovery treatment technique of the present invention, but the waste solutions of the bleach-fixing tank BF and the stabilizing tank substituting for water washing Sb are subjected to the silver recovery treatment by the silver recovery means 80 according to the silver recovery treatment technique of the present invention as described above before they are charged into the stock tank 30. In the automatic processing machine shown in Figure 1, the solutions overflowed from the upper portions of the processing tanks by replenishment of the replenisher are to be processed as the photographic processing waste solution.

Provision of a plural number of silver recovery means 80 or stock tanks 30, and provision of a plural number of treatment means 40, utilizing one or two or more the stock tank (for example, using them alternately as the stock tank and the treatment means), etc., are also included in the present invention. If a certain amount is treated at a time by use of the stock tank 30, the concentrated or dried photographic processing waste solution can be uniformized, and the stock tank 30 is useful as the buffer from the photographic processing tanks to the treatment means.

As a means for transferring the overflowed photographic processing waste solution to the silver recovery means or the stock tank 30, a simple method is to permit it to fall naturally through a guide pipe. However, there may be also provided a means for collecting the heat energy possessed by the photographic processing waste solution by arrangement of heat exchange means in the course of transfer, or alternatively a means for preheating or evaporating the solution of the photographic processing waste solution before collected into the silver recovery means 80 or the stock tank 30 by utilizing the heat energy of the automatic processing machine or the evaporation treatment device as described below. Also, it can be sometimes transferred forcibly by means of a pump 23, etc.

Also, since the components in the photographic processing waste solutions in the respective photographic processing tanks CD, BF and Sb differ from one another, the case of treating separately by preparation of stock tank 30 for each photographic processing tank or for the waste solutions of the processing tanks divided into 2 or 3 or more groups without treating all the photographic processing waste solutions at a time is also included. Particularly, with respect to recovery of silver, it is advantageous to treat the waste solution of the color developing tank CD separately from the waste solutions of the bleach-fixing tank BF and the stabilizing tank substituting for water washing Sb.

Also, by connecting a pipe to the already existing waste solution tank in the automatic processing machine, etc., the waste solution may be transferred forcibly into the stock tank by means of a pump. Further, the waste solution tank of the automatic processing machine itself can be also utilized as the stock tank. In this case, it is preferable to transfer forcibly the waste solution through the pipeline by actuating the pump with detection

of the weight of said stock tank. It is also preferable to have a float floated in the waste solution tank and actuate the pump by detection of the liquid surface at a certain level or higher, because it can be easily set in an existing automatic processing machine.

C).... Treating means

The treating means 40 includes a heating means 41, a treating chamber 42 containing a means for storing the photographic processing waste solution (concentrate) during treatment or after treatment, a means for discharging the photographic processing waste solution which has been treated (concentrate) from the treating chamber 42.

Also, it may be also made an example added with a gas absorbing means 50 and 51 such as a filter, adsorbent, etc., and a means for reutilization of distilled solution 60 including a cooling means of vapor. As the heating means 41, the heat source and the heating (evaporation) means are important, but there exists no reason to limit these to specific ones in application of the present invention, but there may be included the embodiments in which the photographic processing waste solution is heated by utilizing one or two or more combination of effective heat sources, such as electricity, gas, solar heat, etc., to vaporize and concentrate said photographic processing waste solution. Also, various constitutions are possible from one in which the photographic processing waste solution is stored in the treating chamber 42 and heated as a whole to, for example, one in which the photographic processing waste solution is fallen or thrown (including spraying) onto a heated body such as overheated metal plate, etc., to effect evaporation and one in which it is fed quantitatively to the heat source to be processed continuously. Further, the photographic processing waste solution may be evaporated by atomizing photographic

processing waste solution in mist within the treating chamber 42 and applying heated air thereto. Also, the heated air may be thrown into the photographic processing waste solution.

The means for atomization should preferably be one which carries the photographic processing waste solution on a heated whirling gas stream, preferably a spray drying device.

The heating means 41 may be positioned above or internally of the stored photographic processing waste solution or outside of the treating chamber 42, etc., as desired.

Preheating of the waste solution may be performed on the way from the stock tank 30 to the treating chamber 40 by utilizing heat exchange between the waste solution and the vapor generated.

Other than the constitution utilizing the inner kettle as mentioned above, as the discharging means 43, various designs are possible such that the concentrate of the photographic processing waste solution is permitted to be discharged by use of the cischarging means utilizing rotary screw pump or to fall naturally from the bottom of the treating chamber 42 through the valve and recovered by recovering container 45, followed by addition of the carrier to effect solidification treatment.

Also, the concentrate may be added with the absorvable resin or solidifying agent to conduct solidification and the solidified product is discharged. Further, discharging may be carried out through the separating means such as bag filter.

In the evaporation method of the photographic processing waste solution of the present invention, particularly when the heating means 41 contacts directly the photographic processing waste solution such as the heat source built-in quartz tube or electrical heating

plate of nichrome wire, etc., it has been found that the photographic processing waste solution is secured onto the surface of the heating means under the scorched state to lower remarkably heat efficiency in the process of concentrating or drying the photographic processing waste solution. Also, the photographic processing waste solution is liable to be secured on the thermally conductive member which conducts heat from the heat source to the photographic processing waste solution, and further it has been found that corrosion is liable to occur when the waste solution or its vapor contacts directly the portion not related to heating.

Accordingly, the present inventors have conducted various experiments to obtain the following preferable example.

An example was attempted to apply, for example, Teflon working (coating of fluorine resin) onto the heat source in the case when the photographic processing waste solution or its vapor contacts directly the heat source, or to the surface of the thermally conductive portion in the case when the heat source does not directly contact the photographic processing waste solution as shown in Fig. 1. In this example, two 750 W nichrome wire built-in quartz tubes were used, a metal kettle was provided above the quartz tubes and the photographic processing waste solution was placed therein. When the experiment of treating the photographic processing waste solution was conducted by arranging the heating means applied with Teflon working (coating of a fluorine resin) as the means for preventing securing of photographic processing waste solution 44 on the surface of the metal directly into the photographic processing waste solution to be treated, 2 liters of waste solution could be concentrated to 0.5 liter within 1 hour and no securing phenomenon of tar material of the concentrated waste solution was seen over a prolonged use. On the other

hand, on the metal without any working treatment, a tar material was found to be secured to take a long time for concentration of the photographic waste solution for the second time or thereafter, whereby not only heat efficiency was remarkably lowered, but also progress of corrosion was seen at the metal portion.

When the experiments were conducted with Teflon working means other than coating of a fluorine resin, such as binder type, plating type, oil mixing type, heating treatment type, normal temperature wet cloth type, respectively, good results could be obtained.

Also, when the experiment was conducted in the same manner by use of inorgnaic fibers as described in "Collective Composite Material Technology" (published by Sangyo Gijutsu Center, P.213-219, 1976), "New Material 1984" (published by Toray Research Center, P.287-315, 1984) and "Composite Material" (published by Todai Shuppankai, 1984), the same results as described above were obtained.

As shown in Fig. 1, in the case of utilizing an inner kettle, a means for preventing securing or the photographic processing waste solution as described above is applied on the inner side thereof, particularly at the portion where heat of the heating means 41 is transmitted, but it is preferable to apply the means for preventing securing of the photographic processing waste solution on the whole instrument within the treating chamber for prevention of damages of the instruments by corrosion, etc.

Next, the experiment was carried out for an example in which a nichrome wire built-in quartz tube was arranged (not shown) as the heat source at the bottom of the treating chamber 42 in Fig. 1, a liquid layer 44 of, for example, silicone oil was formed as the securing preventing means to slightly the upper portion thereof and the photographic processing waste solution was stored

thereon to carry out heating treatment. As the result, no securing phenomenon of waste solution onto the heat source could be seen to obtain good result similarly as with Teflon working.

The constitution of the treating chamber 42 may be determined corresponding to the heating means 41 as described above, but it is preferably brought to an atmosphere under reduced pressure to lower the boiling point for promoting evaporation of water.

It is preferable that the treating chamber 42 should be constituted so as to store the photographic processing waste solution or the concentrate which has been treated, an inner kettle or inner liner 44 formed of a metal, porcelain or synthetic resin and, by use of a separating means such as bag filter or pack, the treated concentrate should be solidified and taken out together with the inner liner 47 or the bag filter or pack to be discarded or disposed. Other than the constitution utilizing the inner kettle or inner liner 44 as described above, as the discharging means 43, various designs are possible such that the concentrate of the photographic processing waste solution is permitted to fall naturally through a valve from the known discharging device utilizing a rotary screw pump or the bottom of the treating chamber 42 into a vessel containing 1 or 2 or more of the liquid absorbable resin, solidifying agent and drying agent.

The inner liner 44 or pack should preferably be made of a heat resistant and chemical resistant material such as carbon fiber, aramide fiber, Teflon resin fiber, hemp, glass fiber, polyethylene form, polypropylene form, etc.

Also, the concentrate may be added with a liquid absorbable resin, a solidifying agent or a drying agent such as lime, etc., before discharging. Further, it is also preferable to effect discharging through a

separating means such as bag filter, etc.

The gas adsorbing means 50 separates and recovers harmful gases such as hydrogen sulfide, sulfur oxide, or ammonia gas (H_2S, SO_2, NH_3, etc.) contained in the evaporated photographic processing waste solution by utilizing various desulfurization and adsorption technique such as zeolite adsorbent, activated charcoal, etc.

The cooling means 60 performs secondary treatment of the distilled solution subjected to evaporation treatment by the waste solution treating means 40 with activated charcoal, reverse osmosis membrane, UV-ray irradiation, oxidizing agent, etc., to obtain distilled solution, which is utilized in photographic processing solution in the automatic processing machine 10. That is, for example, it is used when utilized as the dissolving solution for the replenisher or the stabilizing solution.

D).... Control

The control in the evaporation treatment device of the photographic processing waste solution of the present invention is important primarily for the respective items of:

(1) discharging of photographic processing waste solution to the silver recovery means 80 or the stock tank 30 and 31;

(2) feeding of the photographic processing waste solution from the stock tank 30 to the treating means 40; and

(3) actuation of the treating means 40, and these items are described in this order.

(1) Discharing of the photographic processing waste solution to the silver recovery means 80 or the stock tank 30:

The amount and the temperature of the photographic processing waste solution in the silver recovery means 80

or the stock tank 30 are detected by the sensor 24, and their informations are successively memoried at the memory portion of the control device 20. Accordingly, when the photographic processing waste solution in the silver recovery means 80 or the stock tank 30 is detected to be under the full state, replenishment of the replenisher is prohibited so that no photographic processing waste solution may not newly discharged, or emergent discharging by means of a pump is effected from the silver recovery means 80 or the stock tank 30 to the treating means 40 following the supplement indicating information of the replenisher. For prevention of erroneous actuation, it is preferable to give the silver recovery means 80 or the stock tank 30 surplus of volume or arrange a plural number of silver recovery means 80, stock tank 30 or preliminary tanks. On the other hand, in the system of treating separately following the kinds of the photographic processing waste solutions without treating all of the photographic processing waste solutions at a time, detection of liquid amounts and temperature, etc., is performed for respective silver recovery means 80 and stock tanks 30.

The temperature detection of the photographic processing waste solution in the stock tank 30 is important as the information of the photographic processing waste solution in the actuation control of the treating means 40 described later, particularly for control of the heating temperature.

(2) Feeding of the photographic processing waste solution from the stock tanks 30 and 31 to the treating means 40:

For feeding control of the photographic processing waste solution from the stock tanks 30 and 31 to the waste solution treating means 40, there are the case when the number of the waste solution treating means 40 is single and the case when it is plural. In the latter

case, further plural number of waste solution treating means 40 are prepared, and 1 or 2 or more of them may sometimes function also as the stock tanks. In such a case, the photographic processing waste solution is discharged as divided into the waste solution treating means 40 prepared in a plural number for each waste solution of the photographic processing tanks similarly as in the case of discharging into the stock tanks as described above, and as a general rule subjected to evaporation treatment by the waste solution treating means 40 thrown.

When the waste solution treating means 40 is single, so that the photographic processing waste solutions stocked separately in the stock tank 30 and 31 may not be mixed with each other, another photographic processing waste solution is fed after completion of the treatment of the preceeding solution.

Feeding of the photographic processing waste solution from the stock tank 30 to the treating means 40 may be performed according to a system in which a constant amount (the amount which can be stored at a time within the waste solution treating means 40) is fed at a time and a system in which it is fed continuously in equal amounts or variable amounts. In the former case, feeding of the photographic processing waste solution from the stock tank 30 to the treating means 40 is controlled following the detection informations of the reduced quantity of the photographic processing waste solution in the stock tank 30 by the sensor 22 and/or the photographic processing waste solution quantity in the treating means 40 by the sensor 24. In this case, feeding may be also controlled following the detected information by a flow meter provided in the photographic processing waste solution feeding pipe from the stock tank 30 to the treating means 40.

In the case of the system of feeding continuously

in equal amounts or variable amounts, the amount of the photographic processing waste solution is controlled according to the temperature of the photographic processing waste solution fed, the temperature of the heating means 41 of the treating means 40 or the treating chamber 42. Alternatively, with the amount of the photographic processing waste solution fed being made always constant, the amount of the photographic processing waste solution within the treating means 40 may be detected by the sensor 24 and the heating temperature of the heating means 41 such as heater may be controlled to be elevated or lowered depending on its amount, or the heating time may be controlled to be increased or decreased.

(3) Actuation of the heating means 40:

Control of actuation of the treating means 40, as also described in the previous item, may be done according to the difference in amount of the photographic processing waste solution fed and the photographic processing waste solution treated, or the amount of the remaining photographic processing waste solution or the amounts of the concentrated photographic processing waste solution.

In the system of feeding the photographic processing waste solution in a constant amount at a time, actuation of the treating means 40 can be controlled by controlling the heating time if the temperature of the photographic processing waste solution fed and the temperature of the heating means 41 or the treating chamber 42 are detected.

Feeding of the photographic processing waste solution to be treated and actuation of the treating means (control of the heating means, discharging of the treated waste solution) can be designed variously such as actuation stopping during discharging, low energy actuation of the heating means during discharging,

treatment simultaneous with discharging on feeding, etc.

In the above operation, the degree of treatment progress of the photographic processing waste solution by the treating means is controlled by the treating time, or otherwise by detection of the viscosity of the photographic processing waste solution, the lower limit level of the photographic processing waste solution within the processing chamber 42, the vapor temperature, pressure, weight, electroconductivity, turbidity, transmission or temperature outside the device, etc., and it is preferable to change the actuation of the photographic processing waste solution treating means 40 to stopping or low energy running at the stage when the photographic processing waste solution has been concentrated to a certain level.

As described above, feeding, treatment (evaporation, concentration), discharging of the photographic processing waste solution are controlled by a variety of items, and various sensors 24, etc., are used for detection of time, viscosity, temperature, pressure, liquid surface level, concentration, electric resistance, weight, etc., corresponding thereto, and the sensors 24, etc., can be mounted at various positions.

In the case of time control, it differs depending on the batch treatment and the continuous throwing treatment, and the time is also different depending on the temperature of the photographic processing waste solution fed.

For measuring the treatment progress by detection of the viscosity of the photographic processing waste solution, various viscometers, such as capillary viscometer, etc., may be employed, or otherwise, for example, a load imposed on a propeller or rod for stirring is detected, or the viscosity is detected by the load imposed on the driving motor when using a bar screw as the discharging means. For detection of viscosity by

utilizing such a rotary screw or a propeller, the treatment completion signal is generated by a certain elevation in rotational loading or reduction in rotational number according to the elevation in viscosity.

For detection of concentration, for example, a light emitter, a reflective plate, a light receiver, etc., is arranged at a predetermined height in the treating chamber and a measuring instrument for measuring transmittance (attenuation degree) of light or refractive index is used. It can be also detected by the change in electrical resistance accompanied with the change in concentration.

For detection of the vapor temperature in the treating chamber 42, although not shown, for example, the device may be constituted such that the liquid surface of the waste solution will be lowered with the evaporation treatment until the heated portion is exposed on the liquid surface at a predetermined level or lower. With such a constitution, the vapor temperature within the treating chamber will be abruptly elevated by the overheating phenomenon from the stage when the heating portion has been exposed, whereby the progress of the waste solution processing can be detected.

Also, by mounting a sensor causing change in electrical resistance depending on presence or absence of the liquid at a predetermined height on the inner wall of the treating chamber 42, the liquid surface level can be also detected. The liquid surface level can be also detected by a mechanical mean by use a float, etc.

For measurement of weight, for example, it can be detected by arranging an electrical or mechanical gravimeter below the inner kettle arranged in the treating chamber 42.

The amount of the vapor generated can be detected by arranging a flow meter in the stage preceding to the

gas adsorbing means, and it can also be detected by measuring the amount of the stored distilled solution (weight, liquid surface height) when the cooling means 60 is provided.

In the latter case, actuation of the waste solution treating means 40 may be changed to stopping or low energy running by detection of the vapor temperature, weight or the temperature outside the device.

In the present invention, "concentration" means reduction of the waste solution volume to one half or less of the volume when exiting from the photographic processing tank, preferably one fourth or less with respect to discarding, more preferably one fifth or less, optimully one tenth or less. By concentration, generation of precipitates or tar, etc., may occur. The liquid as a whole is required to be fluid, and presence of precipitates or sludge may be permissible.

[Examples]

The present invention is described in detail by referring to the following examples, by which the embodiments of the present invention are not limited at all.

The Sakura Color SR paper (produced by Konishiroku Photo industry Co.) was picture printed and then subjected to continuous processing by use of the following processing steps and processing solutions.

Basic processing steps:

(1)	Color developing	38 °C	3 min. 30 sec.
(2)	Bleach-fixing	38 °C	1 min. 30 sec.
(3)	Stabilizing processing	25 °C-35 °C	3 min.
(4)	Drying	75 °C-100 °C	about 2 min.

Processing solution compositions:

[Color developing tank solution]

Benzyl alcohol	15 ml
Ethylene glycol	15 ml
Potassium sulfite	2.0 g

Potassium bromide	1.3 g
Sodium chloride	0.2 g
Potassium carbonate	24.0 g
3-Methyl-4-amino-N-ethyl-N-(β-methanesulfoneamidethyl)aniline sulfate	4.5 g
Fluorescent brightener (4,4'-diaminostilbendisulfonic acid derivative) (trade name: Kaicoll PK-conc, produced by Shinnisso Kako Co.))	1.0 g
Hydroxylamine sulfate	3.0 g
1-Hydroxyethylidene-1,1-diphosphonate	0.4 g
Hydroxyethyliminodiacetic acid	5.0 g
Magnesium chloride hexahydrate	0.7 g
1,2-Dihydroxybenzene-3,5-disulfonic acid-disodium salt	0.2 g

(made up to one liter with addition of water, and adjusted to pH 10.20 with potassium hydroxide and sulfuric acid).

[Color developing replenisher]

Benzyl alcohol	20 ml
Ethylene glycol	20 ml
Potassium sulfite	3.0 g
Potassium carbonate	30.0 g
Hydroxylamine sulfate	4.0 g
3-methyl-4-amino-N-ethyl-N-(β-methanesulfoneamideethyl)aniline sulfate	6.0 g
Fluorescent brightener (4,4'-diaminostilbendisulfonic acid derivative) (trade name: Kaicoll PK-conc, produced by Shinnisso Kako Co.))	2.5 g
1-Hydroxyethylidene-1,1-diphosphonic	

acid	0.5 g
Hydroxyethyliminodiacetic acid	5.0 g
Magnesium chloride hexahydrate	0.8 g
1,2-Dihydroxybenzene-3,5-disulfonic acid disodium salt	0.3 g

(made up to one liter with addition of water, and adjusted to pH 10.70 with potassium hydroxide).

[Bleach-fixing tank solution]

Ferric ammonium ethylenediamine-tetraacetate dihydrate	60.0 g
Ethylenediaminetetraacetic acid	3.0 g
Ammonium thiosulfate (70% solution)	100.0 ml
Ammonium sulfite (40% solution)	27.5 ml

(made up to the total quantity of one liter with addition of water and adjusted to pH 7.1 with pottasium carbonate or glacial acetic acid).

[Bleach-fixing replenisher A]

Ferric ammonium ethylenediamine-tetraacetate dihydrate	260.0 g
Potassium carbonate	42.0 g

(made up to the total quantity of one liter with addition of water, the pH of this solution is 6.7+0.1).

[Bleach-fixing replenisher B]

Ammonium thiosulfate (70% solution)	500.0 ml
Ammonium sulfite (40% solution)	250.0 ml
Ethylenediaminetetraacetic acid	17.0 g
Glacial acetic acid	85.0 ml

(made up to the total quantity of one liter with addition of water, the pH of this solution is 5.3+0.1).

[Stabilizing tank solution substituting for water washing and its replenisher]

Ethylene glycol	1.0 g

1-Hydroxyethylidene-1,1-diphosphonic acid (60% aqueous solution) 1.0 g
Ammonia water (25% aqueous solution of ammonium hydroxide) 2.0 g
(made up to one liter with water and adjusted to pH 7.0 with sulfuric acid).

An automatic processing machine was filled with the above color developing tank solution, the bleach-fixing tank solution and the stabilizing tank solution, and running test was performed while processing the above Sakura Color SR paper sample and replenishing the above color developing replenisher, the bleach-fixing replenishers A, B and the stabilizing replenisher through the constant volume cups every 3 minutes. The replenished amounts were 190 ml as the replenished amount into the color developing tank, each 50 ml of the bleach-fixing replenishers A, B as the supplemented amounts into the bleach-fixing tank and 250 ml of the stabilizing replenisher substituting for water washing as the supplemented amount into the stabilizing bath, respectively per 1 m^2 of the color paper. The stabilizing tank of the automatic processing machine was made a multi-tank countercurrent system, in which the first to the third stabilizing tanks were provided in the direction of the flow of the sample, and replenishment was effected from the final tank, the overflowed solution from the final tank was permitted to flow into the tank in the preceding stage, and further the overflowed solution from this tank was permitted to flow into the tank preceding thereto.

Continuous processing was performed until the total amount replenished of the stabilizing solution substituting for water washing became 3-fold of the stabilizing tank volume.

For the photographic processing waste solution (A) which is the overflowed solution generated by the above

processing, mixed at a ratio of [the overflowed solution of the color developing solution] : [the overflowed solution of the bleach-fixing solution] : [the overflowed solution of the stabilizing solution substituting for water washing] = 3 : 3 : 5, the following treatment was practiced.

Example 1

Evaporation treatment of the photographic processing waste solution (A) was carried out by use of an evaporation kettle having two nichrome wire built-in quartz tubes of 750 W placed therein, and the vapor Q generated was cooled by means of a radiation plate device 62 shown in Fig. 3 to obtain distilled liquid R. Also, the odor was found to be extremely little as compared with the case when using no radiation plate device.

Examples 2 to 7

When the vapor Q obtained by the evaporation treatment in Example 1 was subjected to cooling treatment by use of the cooling means shown in Fig. 4 to Fig. 9, the odor was found to be extremely little in any case similarly as in Example 1 as compared with the case when using no cooling means to give distilled liquid R without any problem. In Fig. 4 to Fig. 6, the photographic processing waste solution had been preliminarily heated, and the evaporation treatment in the evaporation kettle was faster under the same conditions as compared with the case without preliminary heating. Further, the cooling means shown in Fig. 8 was found to be suitable for temperature control of the color developing tank.

Example 8

After evaporation of the 2 liter of the photographic processing waste solution (A) to dryness, the lid 45 was taken off and the dried product was taken out from the evaporation kettle. As the result, it had a strong odor of hydrogen sulfide, with the dried product being sticked to the bottom of the evaporation kettle and also scattered on the wall, whereby all of them could be

removed with difficulty.

Example 9

An inner liner 44 comprising a carbon fiber fabric was covered previously on the bottom of the evaporation kettle, and after evaporation concentration similarly as in Example 1, 20 g of a high liquid absorbable resin (Sumikagel N-100: trade name, produced by Sumitomo Kagaku Co.) was added, and the solidified product was removed together with the inner liner 44 comprising the above fabric to be wholly removed with ease. When the inner portion of the evaporation kettle was observed, it was found to be clean without any trace of the so-called sticking or scattering.

Example 10

Evaporation treatment was carried out with the photographic processing waste solution (A) to be treated fed first into the treating chamber 42 being 2 liter and the heat capacity of the heater 1.5 KW, and the photographic processing waste solution within the treating means 40 was examined when the viscosity at the evaporation temperature by a rotary viscometer was increased by 10%. As the result, it was found to be concentrated to about 3-fold.

Example 11

Evaporation treatment was carried out with the photographic processing waste solution (A) to be treated fed first into the treating chamber 42 being 2 liter and the heat capacity of the heater 1.5 KW, and new feeding of the photographic processing waste solution (A) to be treated was repeated several times when the viscosity by a rotary viscometer was increased by 10%, and then the photographic processing waste solution in the treating means 40 was examined to find that it was concentrated to about 3-fold similarly as in Example 10.

Example 12

When the liquid surface level within the treating

chamber 42 was detected to be leveled down to one tenth, the thickened waste solution was taken out. Also, when the liquid surface level within the treating chamber 42 was detected to be leveled down to one fifth, the photographic processing waste solution (A) to be treated was newly fed. Again, when the liquid level was leveled down to one fifth, the thickened waste solution was taken out.

Example 13

After desilverization treatment of the photographic processing waste solution (A) by use of an electrolytic silver recovering device (produced by San Seiki Industry Ltd., BN-10 type) until the concentration of silver complex salt is reduces to 0.2 g/lit., the waste water was permitted to flow into the stock tank 30. A mixture of such desilverized photographic processing waste solution and overflowed solution of the color developing solution (volume ratio = 3:8) was transferred from the stock tank 30 to the treating means 40. In the treating means 40, the waste solution was subjected to evaporation treatment by use of an evaporation kettle having two nichrome wire built-in quartz tubes of 750 W placed therein. When the evaporation treatment was continuously repeated, it was found that, in the case of evaporation treatment of the photographic processing waste solution which have not been desilverized, silver sulfate was sticked on the bottom of the evaporation kettle, the evaporation efficiency was reduced and hence, after one month, corrosion of the evaporation kettle was caused. On the other hand, in the case of evaporation treatment of the photographic processing waste solution desilverized according to the present invention, such defects were not found at all.

Example 14

Example 13 was repeated in the same manner except for adding sodium sulfide into the photographic

processing waste water in place of employing the electrolytic silver recovering device BN-10 in Example 13 to precipitate silver as silver sulfide. After separation by decantation, the filtrate was permitted to flow into the stock tank 30. Similar good result as in Example 13 was obtained.

Example 15

Example 13 was repeated in the same manner except for carrying out the silver recovering operation for the concentrate which have been subjected to the evaporation treatment. It was found that silver sulfide was sticked to the bottom of the evaporation kettle and, after one month, corrosion of the evaporation kettle was caused. It was also found that, though the same amount of the waste solution having the same silver concentration as in Example 13 was employed, the obtained electrolytic deposited silver was as low as about 20 % of that obtained in Example 13 in which the silver recovery was carried out bofore the evaporation treatment, and further that the electrolytic deposited condition of the electrolytic deposited silver was remarkably poor to cause peel off.

Example 16

After evaporation treatment of the photographic processing waste solution (A) by use of an evaporation kettle having two nichrome wire built-in quartz tubes of 750 W placed therein until the liquid surface level become one tenth, the vapor generated was cooled and the obtained distilled solution was used for preparation of a bleach-fixing solution as a dissolving water. The bleach-fixing solution was employed for processing a ligh-sensitive photographic material. As a result, no problem was caused on the photographic properties and no bumping was seen.

Example 17

The distilled solution obtained by the evaporation

treatment in Example 16 was treated through a column being filled up with Cargon granule-like activated charcoal TYPE SGL (produced by Toyo Cargon Co.) and the obtained secondary treated solution was used for preparation of a color developing solution. The color developing solution was employed for processing a ligh-sensitive photographic material. As a result, no problem was caused on the photographic properties.

Example 18

After irradiation to the distilled solution obtained in Example 16 by use of high pressure mercury lump of 400 W for 4 hours, the secondary treated solution obtained was used for preparation of a bleach-fixing solution and subsecuently the bleach-fixing solution was used for processing a light-sensitive photographic material. As a result, no problem was caused on the photographic properties.

Example 19

The distilled solution obtained by the evaporation treatment in Example 16 was treated by use of an electrolytic device and the obtained secondary treated solution was used for preparation of a stabilizing solution. The stabilizing solution was employed for processing a light-sensitive photographic material. As a result, no problem was caused on the photographic properties.

Example 20

After the treatment of the distilled solution obtained by the evaporation treatment in Example 16 by permitting air to pass through the distilled solution by use of an air pump for 1 hour, the obtained secondary treated solution was used for preparation of a stabilizing solution substituting for water washing and the stabilizing solution substituting for water washing was employed for processing of the light-sensitive photographic material. As a result, no problem was

caused on the photographic properties.

Example 21

Example 1 was repeated in the same manner except for employing a photographic processing waste solution which was prepared by removing the overflowed solution of the stabilizing solution substituting for water washing from the photographic processing waste solution (A). On the other hand, Example 1 was repeated in the same manner for employing a photographic processing waste solution which was prepared by containing the same quantity of water in place of the overflowed solution of the stabilizing solution substituting for water washing of the photographic processing waste water (A). As the resuls, a little sticking and scattering were found in both of them.

As being seen from the comparison with Example 1, in the case of employing the photographic processing waste solution containing the overflowed solution of the stabilizing solution substituting for water wahing, it is understood that so-called sticking and scattering is very little and good results can be obtained.

Example 22

Example 1 was repeated in the same manner except for removing the gas adsorption means 50 in Figure 1 and employing gas adsorbable means 51 being filled up with granule-like activated charcoal (a mixture of activated charcoals type AX and type BX, both are produced by TSURUMICOAL Co. Ltd.). After continuous treatment for 10 hours, amounts of ammonia gas and hydrogen sulfide gas in the discharging section 52 were measured by use of gas detector tube (produced by GASTEC Co.). Subsequently, the same experiment for comparison was carried out for 10 hours and the same measurements of gases were conducted except for removing the cooling means 60.

As a result, in the case of employing the cooling means 60 according to the present invention, the

concentration of ammonia gas was 5 ppm and hydrogen sulfide was 0 ppm. Both of these values are under the value of allowable concentration advised by ACGIH (American Conference of Governmental Industrial Hygienists) (ammonia: 25 ppm, hydrogen sulfide: 10 ppm). Odor was scarecely felt. On the contrary, in the case of removing the cooling means 60, both of the concentrations of ammonia gas and hydrogen sulfide were 0 ppm immediately after the beggining of the eveporation treatment. However, after 1 hour from the beggining of the evaporation treatment, the concentration of ammonia gas was 160 ppm and hydrogen sulfide was 240 ppm. The air around the evaporation treatment device was heavy with bad oder.

Claims:

1. A method for treating a photographic processing waste solution which comprises evaporating a photographic processing waste solution by heating and cooling a vapor generated by the heating by use of a cooling means to obtain a distilled solution.

2. The method according to Claim 1, wherein further comprises obtaining a concentrate of the photographic processing waste solution by the heating and solidifying the concentrate by absorbing on a carrier.

3. The method according to Claim 1, wherein at least one of the following treatments (A) to (I) is applied on the distilled solution: (A) activated charcoal treatment, (B) Ultraviolet-ray irradiation treatment, (C) reverse osmosis treatment, (D) oxidizing agent treatment, (E) electrolytic oxidation treatment, (F) aeration treatment, (G) electrodialysis treatment, (H) redistillation treatment and (I) ion exchange resin treatment.

4. The method according to Claim 1, wherein the distilled solution is reutilized for photographic processing solution.

5. The method according to Claim 1, wherein a gas adsorption treatment is conducted together with distillation.

6. The method according to Claim 1, wherein the gas adsorption treatment is at least one of desulfurization treatment, zeolite adsorption treatment and activated charcoal treatment.

7. The method according to Claim 1, wherein cooling of vapor is performed according to at least one of (A) to (G): (A) treatment with a baffle or a radiation plate, (B) use of the waste solution before heating as the cooling heat medium, (C) cooling treatment carried out in a tank which stocks the waste solution, (D) the above (C) by use of a plural number of stock tanks, (E) utilization

of a fan for air cooling, and (F) cooling treatment effected through heat exchange with the processing tank, replenisher tank or dissolving solution tank of an automatic processing machine.

8. The method according to Claim 1, wherein a silver recovery treatment is carried out before heating the photographic processing waste soluiton.

9. The method according to Claim 8, wherein the silver recovery is carried out according to the electrolytic method, the precipitation method, the metal substitution method or the reduction method.

10. The method according to Claim 2, wherein the carrier is a liquid absorbable resin or a solidifying agent.

11. The method according to Claim 10, wherein at least one of the liquid absorbable resin or the solidifying agent is housed in a pack for waste solution.

12. The method according to Claim 1, wherein the heating of the photographic processing waste solution is controlled by detection of at least one selected from the group shown below:

A Heating time

B Viscosity of the photographic processing waste solution

C Liquid surface level of the photographic processing waste solution

D Temperature of vapor generated from the photographic processing waste solution

E Amount of vapor discharged from a treating means for heating

F Weight of the photographic processing waste solution

G Electroconductivity of the photographic processing waste solution

H Optical density of the photographic processing waste solution.

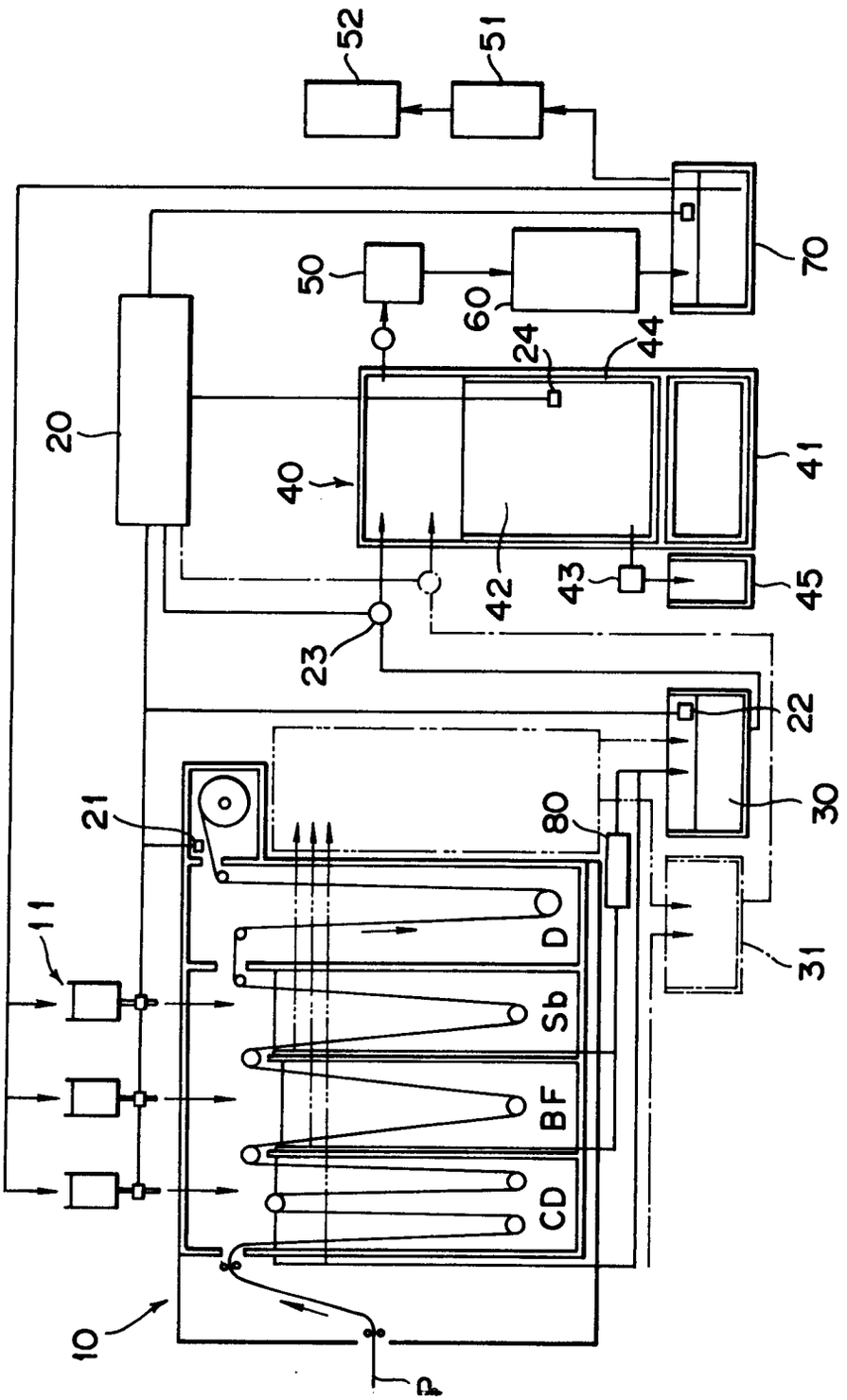
13. The method according to Claim 1, wherein the photographoc processing waste solution contains a waste water of a stabilizing solution substituting for water washing.

14. The method according to Claim 1, wherein the photographoc processing waste solution contains an overflowed solution of a waste water of a stabilizing solution substituting for water washing.

15. A treatment device of a photographic processing waste solution which comprises a treatment tank for performing heating treatment of the photographic processing waste solution, a means for discharging the heated and concentrated solution of the photographic processing waste solution from said treatment tank, a receiving tank for the discharged solution, a means for performing cooling treatment of vapor generated by said heating treatment, a recovering tank for recovering a distilled solution generated by said cooling treatment, and a control means for controlling heating treatment according to the progress of treatment of the waste solution.

16. An automatic photographic processing machine, wherein the treatment device according to Claim 14 is employed.

FIG. 1


52
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24
44
20
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41
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43
45
23
22
21
80
30
11
D
Sb
BF
CD
31
10
P

FIG. 2

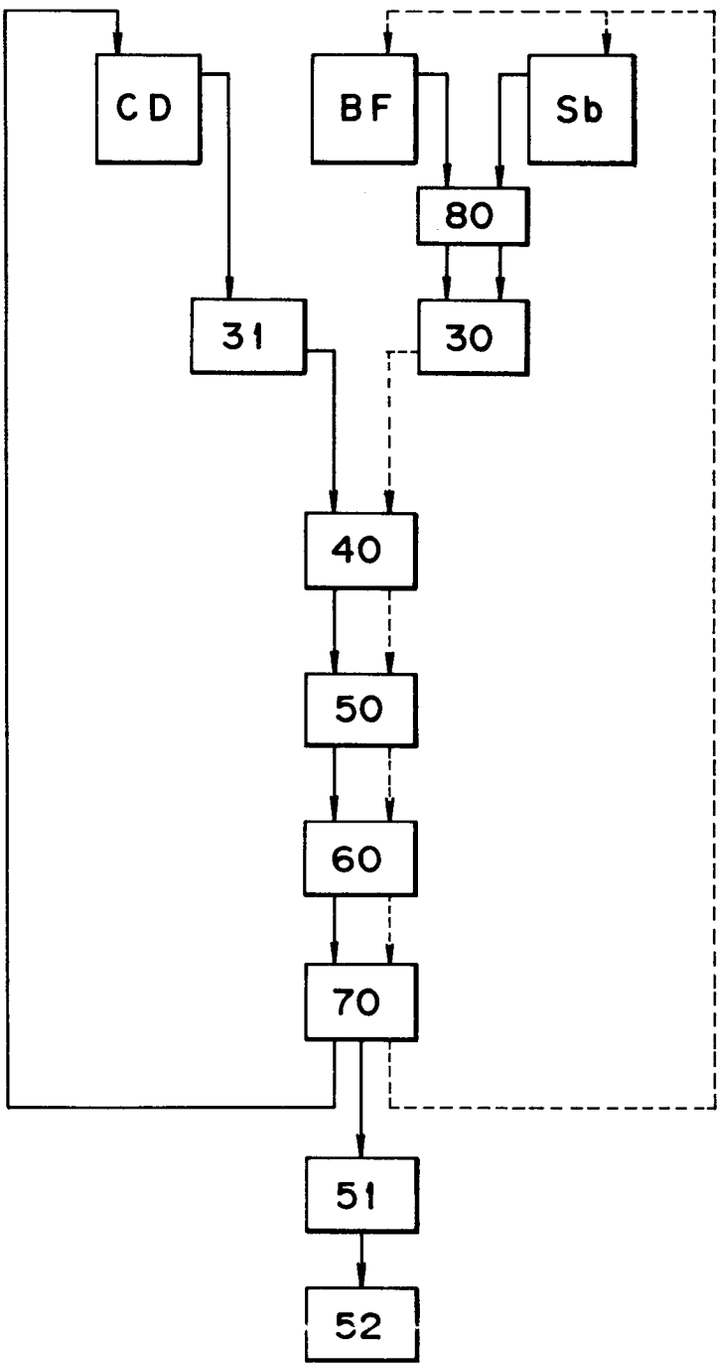

FIG. 3

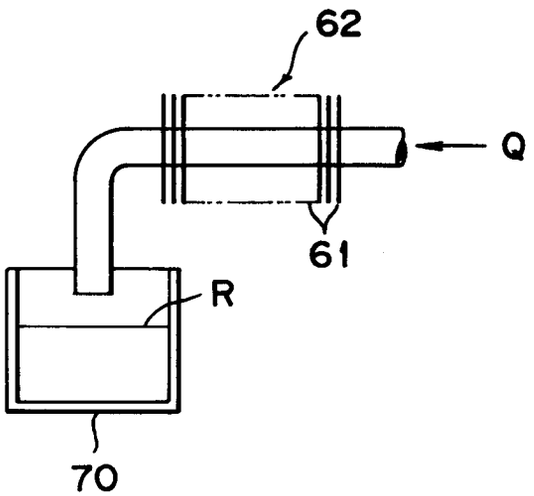

FIG. 4

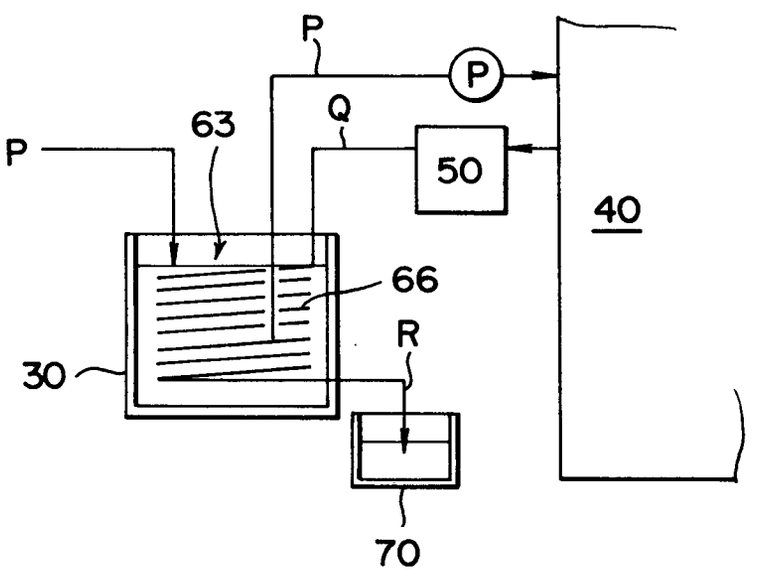

FIG. 5

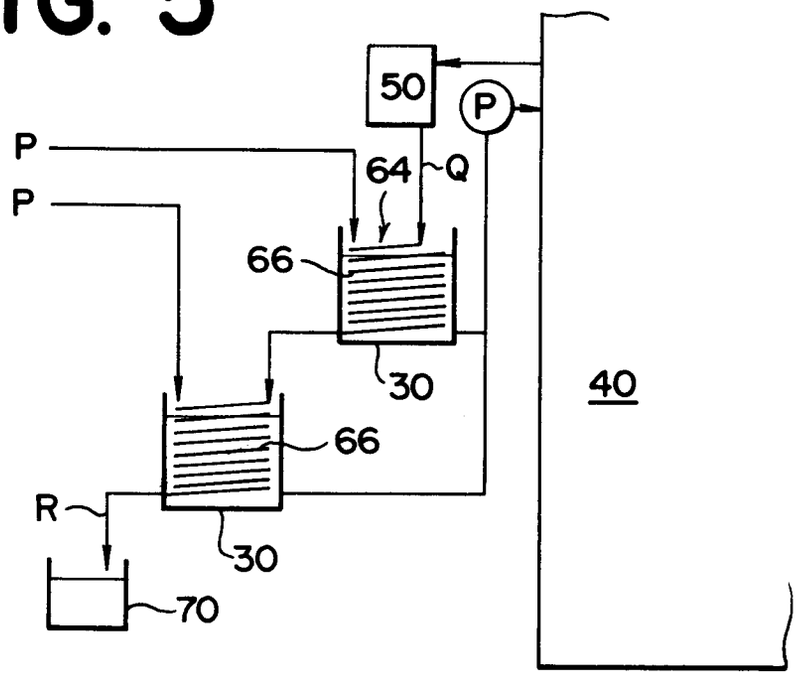

FIG. 6

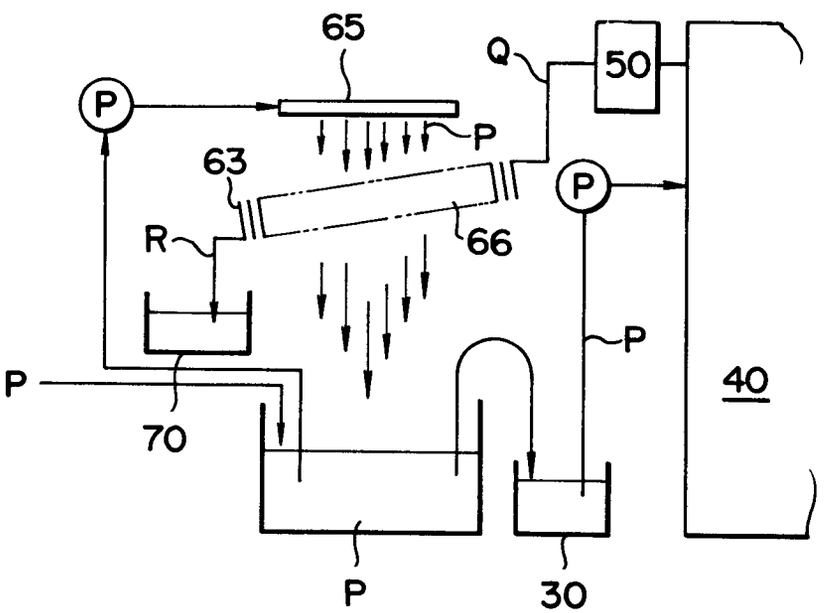

FIG. 7

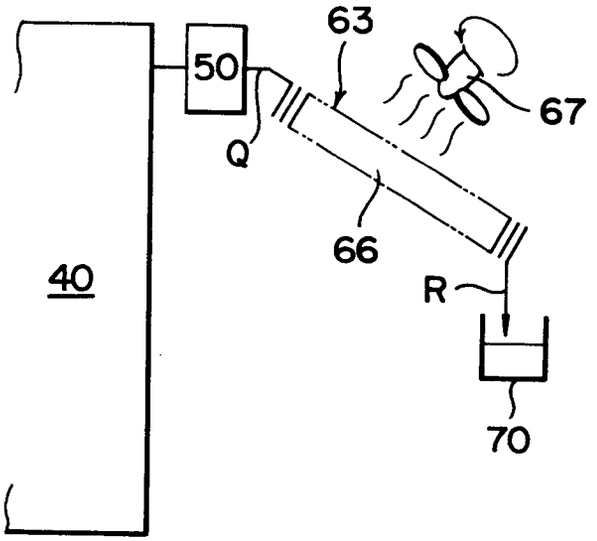

FIG. 8

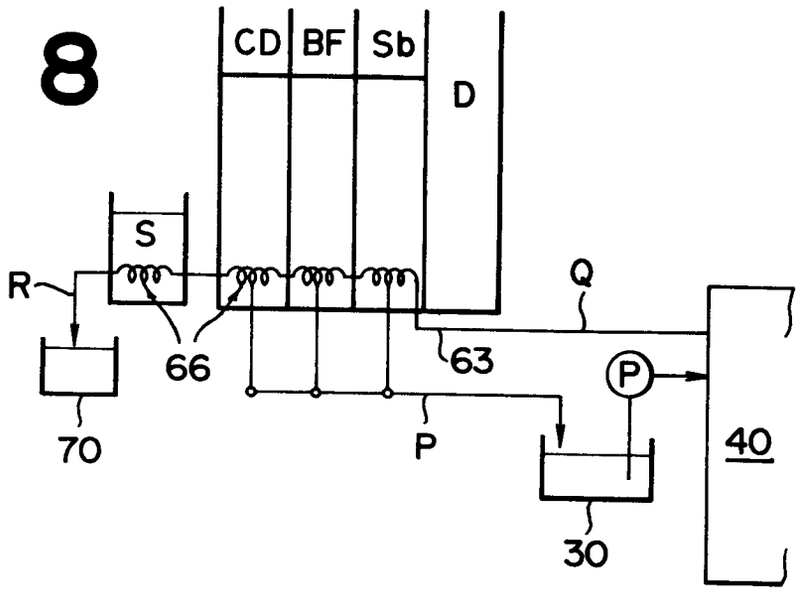

FIG. 9

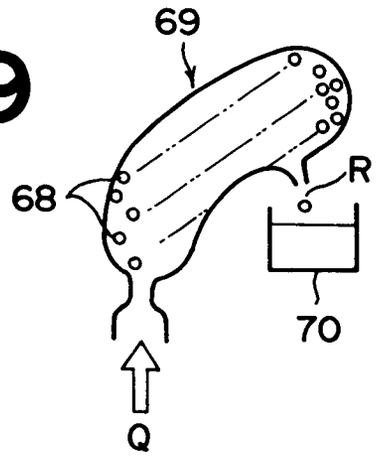

FIG. 10