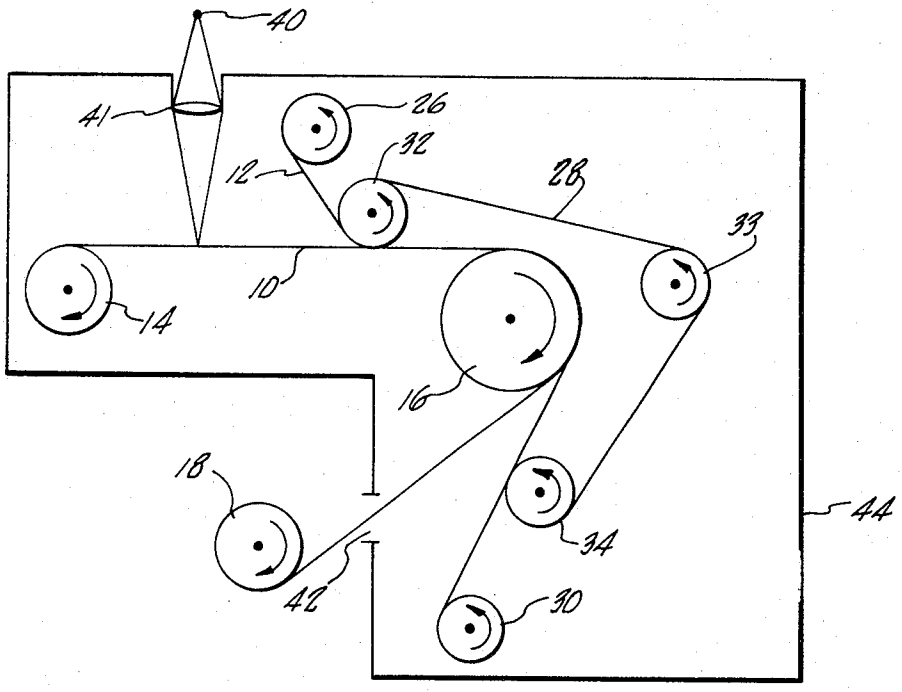
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NON-AQUEOUS SILVER HALIDE PHOTOGRAPHIC EMULSION PROCESSING

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NON-AQUEOUS SILVER HALIDE PHOTOGRAPHIC EMULSION PROCESSING

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This invention relates to a non-aqueous system for processing low speed silver halide silver photographic materials and in particular to processes for developing and stabilizing positive and negative working silver halide materials and for producing stabilized images in silver diffusion transfer materials.

In recent years much effort has been devoted to the investigation of processing exposed silver halide emulsions and especially in the area of high speed processing of such emulsions with the object of speeding or if possible eliminating entirely some of the steps in the course of producing a permanent dry negative or print. In the course of these investigations considerable attention has been devoted to developing agents, fixing and stabilizing agents and vehicles by which they are introduced into the processing reaction, the object being the possibility of uncovering alternatives to classical silver halide processing technology and shorter transition times from exposure to finished product.

As an example, a considerable effort has been devoted to the evolution of self-contained processing systems, such as systems in which all constituents of the processing reaction are incorporated in the emulsion carrying sheet and/or a second processing sheet or in which the processing apparatus has the capability of producing a developed and dry record. Examples of such systems include the Land diffusion transfer systems and developout systems such as typified by U.S. Patent 3,130,000.

As one successor to this technique it has subsequently been found that a non-aqueous system using certain organic compounds such as diols has the capability of supporting a developing reaction. Such a technique is described in a co-pending application of the present assignee, Ser. No. 179,198, filed Mar. 12, 1962.

The complete processing of such emulsions however, requires post-development treatment in order to obtain a permanent record. The usual processes which follow development are rinsing, fixation, hardening, washing and drying. Of these five, fixation, washing and drying are normally required in order to produce a permanent dry negative, though an alternative treatment for prints when extreme permanence is not essential is stabilization and drying.

Such a treatment is necessary because a developd silver halide emulsion normally contains some residual silver halide unaffected by the developer which is held in the emulsion layer. Since this silver halide is still light sensitive, it must be converted either to a water soluble compound and removed by washing (fixation) or to a stable colorless compound (stabilization) if the image is to be permanent. The present invention is concerned with the latter treatment. This type of treatment, namely, the conversion of the remaining silver halide into compounds which can be relatively inert to heat, light and humidity is particularly applicable to the rapid processing of films and papers using small processing machines with heated solutions.

The chemistry of silver halide development and stabilization normally involves the use of solvent to perform several functions. First, a solvent is needed for dissolving the needed reagents such as developers, antifoggants, and stabilizers and provides a vehicle for applying same to the photographic emulsion; second, a solvent provides the medium through which silver ions can move during the development and stabilization reactions. Up to now water has been the only solvent used in completely carrying out these steps.

In contrast the present invention contemplates a system for processing low speed silver halide materials and chemical combinations for use in such processes which do not require water or water-bearing substances to supply the necessary solvent action. This is due to the discovery that the various compounds used in prior art systems are soluble in non-aqueous solvents without significant variations in the quality of the end product. Depending upon the concentration of the various elements of the processing mixtures, the invention contemplates a process not only for development and fixing negative and positive working silver halide materials but also a system for processing diffusion transfer materials. As used herein, low speed emulsions contemplate silver halide mixtures that do not contain silver iodide.

In the case of normal development and stabilization the process contemplates the steps of exposing a low speed silver halide emulsion in which a developing agent has been incorporated to light in order to form a latent image in the emulsion. Thereafter the exposed emulsion is processed by treating it with a mixture comprising a polyhydric alcohol, and an alkali and stabilizer which are soluble in the polyhydric alcohol to perform the functions of developing and stabilizing the image recorded in the emulsion. The treatment can be accomplished in one of several ways as for example by subjecting the exposed emulsion to a processing bath, coating it with a film of liquid, or application by means of a web saturated with the mixture and brought in contact with the emulsion. When the mixture is applied in limited quantities as in the liquid coating or web technique, heat is applied to the emulsion or emulsion-web combination to speed the process.

In the diffusion transfer application the invention again contemplates a process of exposing a low speed silver halide emulsion in which a developer has been incorporated to record a latent image and thereafter treating the emulsion as above. In this case the same formulations as above, i.e., a polyhydric alcohol and an alkali and a silver halide stabilizing agent now function as complexing agents for the diffusion transfer process. In addition, many of the alkalis above when dissolved in a polyhydric alcohol also serve as satisfactory complexing agents. Normally this is accomplished by incorporating a non-aqueous processing mixture as disclosed herein into the transfer or image receiving sheet in which the positive image will ultimately be produced. Again heat is applied at the moment of contact in order to speed the reaction. In a preferred form, the invention contemplates pre-treatment of the image receiving layer in order to provide nucleation sites in the image receiving layer i.e., sites or nuclei around which the diffused and deposited silver grains will grow.

Numerous developing agents have been found to yield satisfactory results in the systems of this invention. Examples include hydroquinone, amidol, phenidone and chlorohydroquinone. Numerous non-sodium compounds usable as stabilizing agents are sufficiently soluble in non-aqueous solvents. Examples of such compounds are potassium thiosulfate, benzene thiosulfonate salts, and salts of mercaptoacetic acid. Examples of alkalis soluble in the solvents used with this system includes many organic bases and certain inorganic compounds such as potassium carbonate and potassium hydroxide. The solvents in which these compounds are soluble are non-volatile polyhydric alcohols or polyols such as ethylene glycol, glycerine and their higher homologues. It has been found that all of the compounds listed above are sufficiently soluble in such polyols to support a developing and fixing reaction as well as a diffusion transfer system.

In addition to its essential solvent function the use of

a polyhydric alcohol has other advantages in that such substances are more readily confined to a system than water bearing materials, and are less susceptible to problems due to varying pressures or humidity. These and other features of the invention will be made more apparent by reference to:

FIG. 1, a schematic representation of one apparatus adapted to the carrying out of the process of this invention.

In that figure a continuous strip **10** of a silver halide emulsion moves from a supply roller **14** over the surface of a rotatable heated drum **16** and is taken up by takeup roller **18**. The surface of the drum is heated by an internal heating coil (not shown) connected to a suitable source of electric power (not shown). A continuous strip of a second sheet **12** from a supply roller **26** is pressed firmly against the first sheet by an endless belt **28** which passes around a portion of the heated drum **16**. The second sheet separates from the first sheet after leaving the heated drum and is taken up by takeup roller **30**. The endless belt is disposed around a drive roller **32** and a pair of idler rollers **33**, **34**. Optionally the endless belt may also include a heating element to apply heat to the second sheet. An image of an object **40** is focused by lens systems **41** on the silver halide emulsion before the second sheet is brought in contact with the first sheet.

As the two sheets move around the heated drum the two layers are pressed together and are heated. The stabilizing compound, alkali and non-aqueous solvent migrate from the layer on the second sheet into the silver halide emulsion. The latent image is made visible by the action of the developer and is subsequently stabilized and can be inspected after it passes through a light tight opening **42** in a box **44** surrounding the transport system.

In a developing and stabilizing process the system contemplates a mixture comprising a non-aqueous solvent and an alkali and a stabilizing agent. To this basic mixture other additives performing such functions as preservatives, anti-foggants and accelerators can be added. As indicated, the solvent that is used is one belonging to the polyol or polyhydric alcohol family. Specific examples include ethylene glycol, $C_2H_4(OH)_2$; glycerol, $C_3H_5(OH)_3$, erythritol, $C_4H_6(OH)_4$; arabital,

$$C_5H_7(OH)_5$$

and sorbitol, $C_6H_8(OH)_6$.

The silver halide stabilizing agents which are added are agents which have been found to have the characteristic of sufficient solubility in any of the above polyols to accomplish their stabilizing function satisfactorily. These agents include potassium thiosulfate, potassium thiocyanate, benzene thiosulfonate salts, thioglycerol, thiourea and salts of mercaptoacetic acid. Alkalis soluble in these alcohols include organic bases such as quarternary ammonium hydroxides and amines and in particular amines such as ethanolamine, diethanolamine, triethanolamine, salts of these ethanolamines and sodium bisulfite and salts of these ethanolamines and acetic acid and inorganic bases such as potassium carbonate and potassium hydroxide.

When applied in a conventional bath to a developed silver halide emulsion the result is a fully stabilized negative or in the case of reversal material, a fully stabilized positive image. In addition to application in the conventional manner several other methods are also possible such as application by means of a slit applicator or roller coater.

In a rapid processing system it is contemplated that the mixture will be incorporated in a web such as is used in an apparatus similar to the one described in conjunction with FIG. 1 or by other means in which the mixture can be applied in small, controlled amounts. In such applications it is contemplated that the developer will be incorporated in the emulsion prior to exposure and the stabilizing formulation applied as above. This imposes

a requirement that the developing agent used also be soluble in a polyhydric alcohol. Developers which have been found to be sufficiently soluble in these alcohols include hydroquinone, methyl hydroquinone, amidol, phenidone, paraphenylene diamine, metol, chlorohydroquinone, pyrogallol and ascorbic acid.

Prior to incorporation in a web for use in a rapid processing application a processing mixture would typically be prepared in the following manner: a stabilizing agent such as potassium thiosulfate and an alkali such as potassium carbonate are added to ethylene glycol. This is done by adding to approximately 11 parts by weight of ethylene glycol heated to approximately 100° C. one part by weight of potassium thiosulfate with stirring. After this solution is complete 0.5 part by weight of potassium carbonate is dissolved in the solution and the mixture is allowed to cool slightly. A porous paper such as filter paper or that used for paper chromatography is bathed in the glycol solution and allowed to remain until saturated. When a web treated with this solution is brought in contact with an exposed low speed silver halide sheet and held there approximately one minute at a temperature of 60° C., the result is a negative of satisfactory contrast and good stability. When similarly applied to a positive working emulsion such as Kodak Autopositive paper, a stabilized direct positive is the result.

By the simple expedient of varying the concentration of the potassium thiosulfate in the processing mixture these same constituents are equally well adaptable to a diffusion transfer system. In this instance only 0.02 part by weight of potassium thiosulfate, that is, approximately one-fiftieth of the original concentration, is used in the processing mixture. When an image receiving layer saturated with the preceding solution is applied to a slow speed silver halide paper and processed for about a minute at approximately 65° C. a positive image is produced on the transfer sheet. As the preceding example illustrates, the same constituents used in a developing and stabilizing process are equally well adapted to a diffusion transfer process by adjusting the concentration of the various components used. In this case the stabilizing agent now functions as a mobilizing or silver transfer agent.

In addition to the preceding formulations, it has been found that the organic bases used as alkalis in the development and stabilization of positive and negative working materials also are capable of functioning as complexing agents in a diffusion transfer process when combined with a polyhydric alcohol. These organic bases include quartenary ammonium hydroxides and amines such as ethanolamine, diethanolamine, triethanolamine, salts of the preceding ethanolamines and sodium bisulfite and salts of the preceding ethanolamines and acetic acid. As illustrated in more detail below, potassium sulfite is also a satisfactory complexing agent.

The diffusion transfer process is enhanced by prior preparation of the image receiving sheet. Such preparation involves providing nucleation regions in the image receiving layer prior to saturation with the polyol-complexing agent mixture of this invention. Nucleation of the sheet support provides means whereby the precipitation of metallic silver can be controlled both as to concentration and disposition in the receiving layer. One example of the way in which the sheet can be nucleated is as follows:

The paper is first bathed in a .001 normal silver nitrate solution and is then blotted free of this liquid and bathed in a .001 normal sodium sulfide solution and is again blotted free of the liquid and dried. This nucleated sheet is then ready for immersion in the various polyol baths by which the processing fluid is incorporated in the image receiving layer.

Other illustrations of possible processing mixtures follow. A nucleated paper prepared according to the preceding technique and bathed in a solution of approximately 11 parts by weight of ethylene glycol and one part by

weight of potassium sulfite provides another image receiving layer for a diffusion transfer system. Contact between this sheet and a developer-incorporating low speed silver halide emulsion for approximately one minute at a temperature of approximately 85° C. produces a positive image in the nucleated sheet. A similarly nucleated sheet bathed in a solution of approximately 11 parts by weight of ethylene glycol and approximately 5 parts by weight of diethanolamine illustrates still another variation in the application of the invention to a diffusion transfer system. By maintaining contact between a nucleated sheet saturated with this mixture and a developer incorporating silver halide emulsion at approximately 60° C. for approximately two minutes a positive image is formed in the nucleated sheet.

As an additional refinement it may be desired to incorporate the processing fluid into a web in a viscous form to avoid the handling of wet materials. The processing liquid can be made viscous by one of several methods well known in current practice in the art such as by adding to the processing solution a gelling agent. When used in this form, heat is an essential requirement in order to melt the solid gel and put the web in condition such that the development and stabilization or transfer reaction may go forward. The preferred ranges of temperature for processing in accordance with this further refinement have been found to be approximately 60° C. to approximately 130° C.

What is contemplated then is a non-aqueous photochemical system especially useful in the rapid processing of low speed silver halide emulsions. This utility encompasses the development and stabilization of low speed silver halide emulsions as well as diffusion transfer applications.

I claim:

1. A non-aqueous process for developing and stabilizing a photographic image comprising the steps of:
   - exposing a low speed photosensitive silver halide emulsion disposed on a sheet to light for the formation of a latent image,
   - applying a developing agent to the exposed emulsion to render the latent image visible and thereafter,
   - processing the emulsion by applying a mixture of a polyhydric alcohol and a stabilizing agent selected from the group consisting of potassium thiosulfate, potassium thiocyanate, benzene thiosulfonate salts, thioglycerol, thiourea and salts of mercaptoacetic acid to the developed emulsion to stabilize the image recorded therein.

2. A non-aqueous process for developing and stabilizing a photographic image comprising the steps of:
   - exposing a low speed photosensitive silver halide emulsion disposed on a sheet to light for the formation of a latent image, the sheet having incorporated therein a developing agent and thereafter,
   - processing the emulsion by applying a mixture of a polyhydric alcohol, an alkali and a stabilizing agent, the alkali being selected from the group consisting of amines, quarternary ammonium hydroxides, potassium carbonate and potassium hydroxide and the stabilizing agent being selected from the group consisting of potassium thiosulfate, benzene thiosulfonate salts, potassium thiocyanate, thioglycerol, thiourea and salts of mercaptoacetic acid to activate the developing agent and develop and stabilize the image recorded therein.

3. A non-aqueous process for developing and stabilizing a photographic image comprising the steps of:
   - exposing a low speed photosensitive silver halide emulsion disposed on a sheet to light for the formation of a latent image, the sheet having incorporated therein a developing agent and thereafter,
   - processing the emulsion by applying a mixture of a polyhydric alcohol, an alkali and a stabilizing agent, the alkali being selected from the group consisting of potassium carbonate, potassium hydroxide, ethanol amine, diethanolamine, triethanolamine, salts of said ethanolamines and sodium bisulfite, and salts of said ethanolamines and acetic acid the stabilizing agent being selected from the group consisting of potassium thiosulfate, benzene thiosulfonate salts, potassium thiocyanate, thioglycerol, thiourea and salts of mercaptoacetic acid to activate the developing agent and develop and stabilize the image recorded therein.

4. A process according to claim 3 in which heat is applied during the processing step to maintain the emulsion and mixture at a temperature in excess of 60° C.

5. A process according to claim 2 wherein the polyhydric alcohol is selected from the group consisting of ethylene glycol, glycerol, erythritol, arabitol and sorbitol.

6. A non-aqueous silver diffusion transfer process comprising the steps of:
   - exposing a low speed photosensitive silver halide emulsion disposed on a first sheet to light for the formation of a latent image, the first sheet having incorporated therein a developing agent,
   - contacting the emulsion side of the first sheet with a second sheet into which has been incorporated a polyhydric alcohol and a complexing agent selected from the group consisting of potassium sulfite and the amines, and
   - applying heat to the contacted sheets whereby the complexing agent is transferred to the first sheet, the developing agent is activated, a portion of the silver halide in the emulsion is dissolved in the complexing agent and an image-wise transfer of silver to the second sheet is completed.

7. A diffusion transfer process according to claim 5 wherein the complexing agent is a mixture of an alkali and a silver transfer agent, the alkali being selected from the group consisting of amines, quaternary ammonium hydroxides, potassium carbonate and potassium hydroxide and the silver transfer agent being selected from the group consisting of potassium thiosulfate, benzene thiosulfonate salts, potassium thiocyanate, thioglycerol, thiourea and salts of mercaptoacetic acid.

8. A non-aqueous silver diffusion transfer process comprising the steps of:
   - exposing a low speed photosensitive silver halide emulsion disposed on a first sheet to light for the formation of a latent image, the first sheet having incorporated therein a developing agent,
   - contacting the emulsion side of the first sheet with a second sheet into which has been incorporated a polyhydric alcohol and a complexing agent selected from the group consisting of potassium sulfite, ethanolamine, diethanolamine, triethanolamine, salts of said ethanolamines and sodium bisulfite, and salts of said ethanolamines and acetic acid, and
   - applying heat to the contacted sheets whereby the complexing agent is transferred to the first sheet, the developing agent is activated, a portion of the silver halide in the emulsion is dissolved in the complexing agent and an image-wise transfer of silver to the second sheet is completed.

9. A process according to claim 6 in which the second sheet has been nucleated prior to exposure by a process comprising the steps of:
   - bathing the sheet in a dilute silver nitrate solution,
   - bathing the sheet in a dilute sodium sulfide solution, and thereafter
   - drying the sheet.

10. A process according to claim 6 in which the heat supplied to the contacted sheets is sufficient to maintain the temperature of the sheets in excess of 60° C.

11. A process according to claim 6 in which the polyhydric alcohol is selected from the group consisting of ethylene glycol, glycerol, erythritol, arabitol and sorbitol.

12. A composition of matter for use in stabilizing low speed photosensitive silver halide emulsions comprising a mixture of a polyhydric alcohol, an alkali and a silver halide stabilizing agent, the alkali being selected from the

group consisting of amines, quaternary ammonium hydroxides, potassium carbonate and potassium hydroxide and the stabilizing agent being selected from the group consisting of potassium thiosulfate, potassium thiocyanate, benzene thiosulfonate salts, thioglycerol, thiourea and salts of mercaptoacetic acid.

13. A composition of matter for use in stabilizing low speed photosensitive silver halide emulsions comprising a mixture of a polyhydric alcohol, an alkali and a silver halide stabilizing agent, the alkali being selected from the group consisting of potassium carbonate, potassium hydroxide, ethanolamine, diethanolamine, triethanolamine, salts of said ethanolamines and sodium bisulfite, and salts of said ethanolamines and acetic acid and the stabilizing agent being selected from the group consisting of potassium thiosulfate, benzene thiosulfonate salts, potassium thiocyanate, thioglycerol, thiourea and salts of mercaptoacetic acid to activate the developing agent and develop and stabilize the image recorded therein.

14. A composition of matter according to claim **12** in which the polyhydric alcohol is selected from the class comprising ethylene glycol, glycerol, erythritol, arabitol and sorbitol.

15. A composition of matter for use with a low speed silver halide emulsion in a silver diffusion transfer reversal system comprising a mixture of a polyhydric alcohol and a complexing agent selected from the group consisting of potassium sulfite and the amines.

16. A composition of matter for use with a low speed silver halide emulsion in a silver diffusion transfer reversal system comprising a mixture of a polyhydric alcohol, an alkali and a silver transfer agent, the alkali being selected from the group consisting of amines, quaternary ammonium hydroxides, potassium carbonate and potassium hydroxide and the silver transfer agent being selected from the group consisting of potassium thiosulfate, benzene thiosulfonate salts, potassium thiocyanate, thioglycerol, thiourea and salts of mercaptoacetic acid.

17. A composition of matter for use with a low speed silver halide emulsion in a silver diffusion transfer reversal system comprising a mixture of a polyhydric alcohol and a complexing agent selected from the group consisting of potassium sulfite, ethanolamine, diethanolamine, triethanolamine, salts of said ethanolamines and sodium bisulfite, and salts of said ethanolamines and acetic acid.

18. A composition of matter according to claim **15** in which the polyhydric alcohol is selected from the class comprising ethylene glycol, glycerol, erythritol, arabitol and sorbitol.

References Cited

UNITED STATES PATENTS

3,186,843 6/1965 Hass ..... 96—66

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