Patented Nov. 12, 1940 2,220,929

UNITED STATES PATENT OFFICE

2,220,929

PHOTOGRAPHIC DEVELOPING SOLUTIONS CONTAINING AROMATIC HYDRAZINES, THEIR PREPARATION AND USE

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No Drawing. Application October 16, 1939, Serial No. 299,762

19 Claims. (Cl. 95—88)

This invention relates to the solubilization of primary aromatic hydrazines. More particularly it relates to photography and more specifically to new developing solutions for use in photographic processes, especially in color photography. Still more particularly it relates to methods for solubilizing aromatic hydrazines for use in photographic processing solutions.

The relative insolubility of primary aromatic hydrazines in aqueous solutions has prevented their use as photographic developing agents. E. Votocek (British Journal of Photography, September 30, 1898, pp. 633—634) first pointed out this difficulty and proposed that it be overcome by introducing solubilizing groups such as sulfonic acid groups into the hydrazines. Caldwell (U. S. 1,082,622) solubilized aromatic hydrazines by forming their alkali metal sulfites. There has not, however, appeared any disclosure of a practical method of making neutral or basic aqueous solutions of aromatic hydrazines which does not involve an undesirable change in their chemical nature or which does not involve the addition of undesirably large quantities of a solubilizing agent. The introduction of known solubilizing groups, e. g. sulfonic acid or sulfonate groups and carboxylic acid or carboxylate groups into hydrazines cuts down developing power.

This invention has for an object the preparation of aqueous solutions of primary aromatic hydrazines, particularly those which are normally insoluble or nearly insoluble in aqueous systems. A further object is to provide concentrated neutral or alkaline aqueous solutions of primary aromatic hydrazines. A still further object is to provide aqueous alkaline developer solutions containing primary aromatic hydrazines. Still other objects will appear hereinafter.

The above objects are attained and the disadvantages overcome by the preparation and use of a photographic developer formed by solubilizing a primary aromatic hydrazine in an aqueous solution of a long chain surface active polar compound containing a hydrophylic group and a hydrophobic group comprising a hydrocarbon group of 8 or more carbon atoms and preferably 12 to 18 carbon atoms, and preferably in a solution containing from 0.1 to 2% of, and more preferably from 0.1 to 0.5% of, such compounds.

Suitable surface active agents include the water soluble salts of the long chain aliphatic carboxylic acids, long chain aliphatic sulfonic acids, long chain aliphatic sulfates, mineral oil sulfonates, long chain alkylated aromatic sulfonic acids, long chain aliphatic hydrocarbon substituted betaines, etc. Suitable salt-forming groups are alkali metal, ammonium, quaternary ammonium and hydrocarbon substituted ammonium or amine.

The solutions are preferably neutral or basic but in some cases may be weakly acid. The aromatic hydrazines are somewhat soluble in acid solutions, however, hence the important embodiment of this invention is concerned with neutral and alkaline developer solutions.

The resulting solutions may be used in many of the reactions where it is customary to use organic solvent solutions of the hydrazines. The solutions are especially useful in photographic developing processes and solutions. Although the hydrazines are soluble in weakly acidic solutions, it is only in their neutral and basic solutions that they exhibit good development characteristics.

It has been discovered that surface active agents of the type above given exert a peculiar and wholly unexpected effect on primary aromatic hydrazines causing them to form clear solutions in aqueous systems and remain in solution even when made strongly alkaline. This is particularly surprising since phenylhydrazine, for instance, is soluble in water to a slight extent. When, however, phenylhydrazine is poured into a dilute aqueous solution of sodium oleate, e. g. 1% to 0.1%, it dissolves in a wide range of proportions, e. g. up to 50% by weight with only gentle mixing. The resulting solution is clear, transparent, colorless and does not have the appearance of an emulsion. While it is difficult to explain the nature of this phenomenon, it has been found that it is by no means of general application since basic aromatic compounds such as the aromatic amines and the like are not similarly solubilized to form clear solutions. Amines such as aniline, dimethylaniline and p-aminodimethylaniline, for example, are not readily dissolved by very dilute sodium oleate solutions of from 1 to 0.1% concentration, but are emulsified if shaken or stirred vigorously. Primary aromatic hydrazines in general, on the other hand, exhibit this peculiar behavior of dissolving in very dilute soap solutions. Some of the hydrazines, for example, those which are highly substituted with nitro groups, are almost entirely water insoluble, yet they may be solubilized in like manner. The solutions of some hydrazines are not always perfectly transparent, nevertheless, they contain an appreciable amount of hydrazine in a solubilized state. Thus, it is believed that the process may be applied to solubilizing considerable quantities of all primary hydrazines.

The preferred agents for solubilizing these hy-

drazines are anion active compounds. More specifically they are water soluble salts of monovalent aliphatic acids of the type R—X⁻, where R is an acyclic hydrocarbon radical of at least 12 carbon atoms and X is chosen from —COO⁻ and —SO_3. The salt-forming group may be an alkali metal, amine or any other group commonly found in such compounds, or the compound may be in the form of an inner salt such as the long-chain aliphatic hydrocarbon betaines. The compounds mentioned apparently do not form specific combinations with the hydrazines because of the wide variation of concentrations possible in their use. It is also evident that a chemical change does not occur since both compounds can be recovered from the solution.

Two methods are available for preparing these solubilized hydrazine solutions. One consists in adding a hydrazine to an aqueous medium having a pH of approximately 7 or greater, then adding a small amount of a 2% solution of the solubilizing agent so that the concentration of the solubilizing agent is less than 1%, and heating until solution is complete. It may then be cooled without depositing any solids. The second method consists in dissolving the aromatic hydrazine as its mineral acid salt (hydrochloride, sulfate, etc.) in water, adding the solubilizing agent as a 2% solution and heating while an alkaline solution is added until the pH is as desired (approximately 7 or greater). The solution may then be cooled without depositing any solids. Either method produces the same solution.

The invention will be further understood but is not intended to be limited by the following examples:

Example I

An aqueous solution comprising 1 part by weight of sodium oleate per 100 parts of solution is stirred slowly while phenylhydrazine is poured in. Any desired strength of solution may be prepared in this manner by addition of the calculated amount of phenylhydrazine. Such solutions, containing not over 50% by weight of phenylhydrazine may be diluted to any desired degree by stirring while water is added. A small amount of an alkali metal acetate is added and the solution used for developing films.

Example II

To an aqueous solution containing 0.2 part of sodium oleate per 10 parts of solution is added 4 parts of phenylhydrazine and the solution diluted with 986 parts of water containing 12 parts of sodium phosphate. This solution can then be used as a photographic developer.

Example III

Three parts of alpha-naphthylhydrazine are added to 80 parts of hot water. Eighteen parts of a 2% aqueous sodium oleate solution are added and the mixture warmed and stirred until solution is complete. It is then cooled to 10° C. and will remain in solution. Such a solution may be diluted with 400 parts of water containing 6 parts of sodium carbonate and used as a developing solution for photographic films.

Example IV

Three parts of p-nitrophenylhydrazine hydrochloride are dissolved in 74 parts of boiling water. To this is added 15 parts of hot 2% aqueous sodium oleate solution, then 10 parts of water containing 1 part of sodium carbonate. As soon as solution is complete, it is cooled to 20° C. and shows no tendency to precipitate even after two days. When this solution is diluted with 400 parts of water containing 8 parts of sodium carbonate it may be used as a photographic developing solution.

Concentrated solutions of the type described above may be diluted with water to any desired strength without showing any tendency to form a precipitate. The pH of these developing solutions may be controlled between approximately 7 and 12 by addition of more or less alkaline salts such as carbonates, sulfites, phosphates, acetates, phthalates, citrates or the like, alkali hydroxides, ammonia or amines without affecting the solution.

The invention is not limited to the hydrazines set forth in the preceding examples. Among the hydrazines which may be solubilized in this manner are the following, although the invention is not limited to solubilization of these but extends to all primary aromatic hydrazines:

Tolylhydrazines
Nitrophenylhydrazines
Bromophenylhydrazines
Chlorophenylhydrazines
Chloronaphthylhydrazines
Bromonaphthylhydrazines
p-Diphenylhydrazine
p,p'-Diphenyldihydrazines
Methoxyphenylhydrazines
p-Carbethoxyphenylhydrazines

All of these hydrazines will give transparent solutions when solubilized as above except those which are normally very slightly soluble in water such as the nitrophenylhydrazines, naphthylhydrazine, and diphenylhydrazines. These latter compounds, however, form slightly cloudy solutions in aqueous sodium oleate but show no tendency to precipitate even after two days.

Foam breaking compounds or materials may be added if desired; in general they are employed in low concentrations, e. g. 2 to 15 drops of 5% solution per liter of developer. Suitable foam breakers include saturated aliphatic alcohols of at least 6 carbon atoms and lower aliphatic carboxylic acid esters thereof, e. g. hexyl alcohol, hexyl acetate, octyl alcohol, octyl acetate, 2-ethyl hexyl acetate, etc.

In place of the surface active agents described in the examples may be substituted a large number of other compounds which fall within the classes of compounds set forth above. Suitable agents include the water-soluble alkali metal, ammonium and amine salts of stearic, palmitic, oleic, arachidic, eleostearic, ricinoleic, 12-hydroxystearic, myristic, linoleic acid, the same salts of primary or secondary aliphatic hydrocarbon sulfonic acids containing at least 8 carbon atoms, e. g. of dodecane, tetradecane, octadecane, and 3,10-diethyltridecanesulfonic acids, mineral oil sulfonates, etc.; the alkali metal, ammonium and amine salts of alkylated aromatic sulfonic acids, e. g. containing a carbon chain of at least 8 carbon atoms, p-dodecyl-phenolsulfonic, oleo-p-anisidinesulfonic, etc. acids, alkyl sulfates of 8 to 24 carbon atoms, e. g. dodecyl-, tetradecyl-, and octadecyl-sulfate, etc., oleyl sulfate, diethyl cyclohexylamine dodecyl-sulfate, etc. As examples of suitable salt-forming groups, mention is made of sodium, potassium, ammonium, alkylolamine, e. g. mono-, di- and tri-ethanolamine, methyl and ethyl amines, etc. Reaction products of long chain carboxylic acids

with taurine, isethionic acid, etc. are also useful. As examples of suitable betaine compounds which may be used are C-(n-hexadecyl)-α-betaine, C-(n-dodecyl)-α-betaine, and the salts of the corresponding open chain betaine compounds. Mixtures of the above agents may be also used.

Surface active agents of the type known as "Turkey red oil" are mixtures containing several different compounds and, inasmuch as some of these are salts of long chain aliphatic acids, their sulfonates and sulfates such as oleic acid and its sulfonate, ricinoleic acid and its sulfate, oleostearic acid, hydroxystearic acid and its sulfate, etc., these mixtures may be used for solubilization of the aromatic hydrazines. It is sometimes necessary to use larger amounts of these mixtures as the actual concentration of the useful surface active agents in these is lower than in pure soap solutions, but the concentration of active solubilizing agent for a satisfactory developer solution should not exceed 1%.

The preferred compounds are the alkali metal salts of the general formula R—X—M, wherein R is an n-alkane radical of at least 12 carbon atoms, X is a —COO— or —SO_3— group, and M is sodium or potassium.

Solubilization of aromatic hydrazines by this process apparently is not a simple dispersion phenomenon, since phenylhydrazine can be made to form a perfectly clear solution in dilute sodium oleate solution in a wide range of proportions, e. g. up to 50% by weight without showing any loss of clarity in the solution. Also the preferred agents used in this process include only a limited group of the large class known to be good dispersing or wetting agents in other common dispersion processes. This unusual solubilizing effect is not observed in the case of water-insoluble primary aromatic amines and certain water-insoluble amino developing agents; this being the case the phenomenon is not a general one that can be applied to any insoluble developing agent and in fact it is only with primary aromatic hydrazine developing agents that this striking and wholly unexpected solubilizing effect has been observed.

In this solubilizing process it is possible that a loose molecular combination occurs between one or more hydrazine molecules and one of the solubilizing agents since the hydrazine may be in large excess. If such combinations are formed it seems that their relative solubilities closely correspond to the relative solubilities of the hydrazines themselves in water without solubilizing agents. The foregoing is only a theory and the invention is not to be considered as limited thereby.

The developer solutions of this invention may be used in the same manner as hydrazine developer solutions of the prior art have been used. Thus, they may be used for developing exposed or latent silver halide images such as silver chloride or bromide images, or reversed images or bleached images such as silver ferrocyanide images. The developer solutions hereof are particularly useful in the color developing processes set forth in the application of David W. Woodward and David M. McQueen, Serial No. 299,760, entitled Photographic processes, filed upon an even date herewith.

This invention makes it possible to prepare aqueous solutions of a valuable class of chemical reagents that are normally water-insoluble. The aromatic hydrazines have long been neglected as developing agents, probably because of the difficulty in preparing their neutral and basic aqueous solutions.

Aromatic hydrazines may be dissolved in dilute mineral acid solutions or their mineral acid salts may be prepared and these dissolved in water. Such solutions, however, when made neutral or basic rapidly precipitate the hydrazine. Hitherto it has only been possible to dissolve primary aromatic hydrazines in basic solutions by a change in their chemical structure such as the introduction of an acid group or a metal sulfite group or the like. Such a method has limited application as these groups cannot always be readily introduced into the molecule, and further they introduce undesirable effects in many cases and in some destroy their utility as photographic developing agents, etc. This invention has the marked advantage that it provides an easy and general method for solubilizing primary aromatic hydrazines in neutral and alkaline solution without affecting their chemical reactivity.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiment hereof except as defined by the appended claims.

I claim:

1. An aqueous photographic developing solution containing a primary aromatic hydrazine dissolved in a solution of a long chain surface active polar compound.

2. An aqueous photographic developing solution containing a primary aromatic hydrazine dissolved in a 0.1 to 2% solution of a long chain surface active polar compound containing a hydrophylic group and a hydrophobic group of at least 8 carbon atoms.

3. An aqueous photographic developing solution having a pH of at least 7 containing a primary aromatic hydrazine dissolved in a 0.1 to 1% solution of a long chain surface active polar compound containing a hydrophylic group and a hydrophobic group of at least 8 carbon atoms.

4. An aqueous photographic developing solution containing a primary aromatic hydrazine dissolved in a 0.1 to 1% solution of a long chain surface active polar compound containing a hydrophylic group and a hydrophobic group comprising an aliphatic hydrocarbon radical of at least 8 carbon atoms.

5. An aqueous alkaline photographic developing solution containing a primary aromatic hydrazine dissolved in a 0.1 to 1% solution of a long chain surface active polar compound containing a hydrophylic group and a hydrophobic group comprising an aliphatic hydrocarbon radical of at least 8 carbon atoms.

6. The process of developing a silver salt image in a developing solution of the type set forth in claim 1.

7. An aqueous photographic developing solution having a pH of at least 7 containing an aromatic hydrazine dissolved in a 0.1 to 1% solution of a water soluble salt of a fatty acid of 12 to 18 carbon atoms.

8. An aqueous photographic developing solution having a pH of at least 7 containing an aromatic hydrazine dissolved in a 0.1 to 1% solution of an alkali metal salt of a fatty acid of 12 to 18 carbon atoms.

9. An aqueous photographic developing solution having a pH of at least 7 containing an aromatic hydrazine dissolved in a 0.1 to 1% solu-

tion of a water soluble salt of a long chain aliphatic sulfonic acid.

10. An aqueous photographic developing solution having a pH of at least 7 containing an aromatic hydrazine dissolved in a 0.1 to 1% solution of an alkali metal salt of a long chain aliphatic sulfonic acid.

11. An aqueous photographic developing solution having a pH of at least 7 containing a primary aromatic hydrazine dissolved in a 0.1 to 1% solution of a long chain surface active polar compound containing a hydrophylic group and a hydrophobic group of at least 8 carbon atoms, and an alkaline salt.

12. A process for solubilizing primary aromatic hydrazines comprising stirring said hydrazine in an aqueous solution of a pH of 7 to 12 containing a basic salt and an alkali metal salt of a fatty acid containing 12 to 18 carbon atoms while heating if necessary until solution is complete.

13. A process for solubilizing primary aromatic hydrazines comprising stirring said hydrazine in an equeous solution of a pH of 7 to 12 containing an alkali metal salt of a fatty acid containing 12 to 18 carbon atoms until solution is complete.

14. A solution as set forth in claim 7 wherein the salt is sodium oleate.

15. A solution as set forth in claim 7 wherein the salt is triethanolamine stearate.

16. A solution as set forth in claim 5 wherein the surface active compound is sodium paradodecylphenolsulfonate.

17. A solution as set forth in claim 1 wherein the hydrazine is monophenylhydrazine.

18. A solution as set forth in claim 1 wherein the hydrazine is para-nitrophenylhydrazine.

19. A solution as set forth in claim 1 wherein the hydrazine is para,para'-diphenyldihydrazine.

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