

United States Patent [19]

Swan et al.

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[54] **AZODICARBONAMIDES AS
PHOTOGRAPHIC BLEACHING AGENTS**

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[22] Filed: **Apr. 10, 1972**

[21] Appl. No.: **242,757**

[30] **Foreign Application Priority Data**

Apr. 14, 1971 Great Britain 9,420/71

[52] U.S. Cl. **96/60 R, 96/22, 96/60 BF**

[51] Int. Cl. **G03c 5/32, G03c 7/16**

[58] **Field of Search..... 96/60, 60 BF, 22, 96/56**

[56] **References Cited**

UNITED STATES PATENTS

3,655,391 4/1972 Merli et al. 96/66.5
3,702,248 11/1972 Alcock et al. 96/60 R

FOREIGN PATENTS OR APPLICATIONS

336,527 3/1959 Switzerland 96/60 R

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Attorney—Kinney, Alexander, Sell, Steldt & DeLaHunt

[57] **ABSTRACT**

Pollution and toxicity problems associated with conventional photographic bleach solutions may be reduced or eliminated by employing an azodicarbonamide as the bleaching agent.

42 Claims, No Drawings

AZODICARBONAMIDES AS PHOTOGRAPHIC BLEACHING AGENTS

This invention relates to the bleaching of silver developed from photographic silver halide emulsions. In particular the invention relates to a process for bleaching developed photographic silver halide emulsions and to bleaching baths for use in this bleaching process.

It is essential to remove developed silver from photographic silver halide emulsions at various stages during the processing of certain photographic materials. For example, one method of making black and white positive images is to develop the exposed emulsion, bleach out the developed silver, then expose the emulsion to light again to enable the remaining non-exposed silver halide to be developed which is then developed and fixed to give the desired positive image. Another instance where bleaching is required is in the processing of color reversal and color negative films since developed silver must be removed from the emulsion before the various dyes can be seen in their correct balance and intensity.

The required bleaching is usually achieved by treating the photographic material in a bleaching bath containing a ferricyanide such as potassium ferricyanide. While these bleaching baths give good results they have the disadvantage that the ferricyanide is highly toxic. They must, therefore, be used with great care and, after use, cannot simply be thrown away. In practice, even with great care, their use constitutes a serious potential threat of pollution. The threat is particularly serious because these ferricyanides are very stable and so can accumulate. It would, therefore, be a great advantage to be able to bleach developed silver from photographic emulsions without having to use a highly toxic, pollution-causing bleaching agent.

It is, therefore, an object of the invention to provide a method for the bleaching of silver in photographic elements which employs a bleaching agent which is substantially non-toxic and non-polluting.

It is another object of the invention to provide a photographic processing solution capable of bleaching silver from photographic elements and which includes a substantially non-toxic, non-polluting bleaching agent.

It is yet another object of the invention to provide a photographic bleach-fix solution employing a substantially non-toxic, non-polluting bleaching agent.

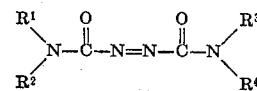
Briefly, the invention in one embodiment relates to a process for bleaching photographically developed silver comprising contacting the developed silver with an aqueous processing solution containing, as a bleaching agent, an azodicarbonamide. Azodicarbonamides are substantially non-toxic, and so no special precautions need to be taken during their use or for their disposal. In addition they have the advantage that they fairly rapidly decompose when in solution and so they can be exhausted into a drainage system and will not cause a serious build-up in concentration in streams and rivers.

Azodicarbonamides are electron acceptors, and so act as oxidizing agents for developed silver, oxidizing the developed metallic silver. When oxidizing developed metallic silver, the azodicarbonamides become reduced, the double bond between the two nitrogen atoms of the azo group opening and becoming saturated. As noted above, azodicarbonamides as a class decompose fairly readily, particularly when in solution. Their manner of decomposition is complicated but it

appears that they decompose to nitrogen, a urea and hydrazine derivatives, and these decomposition products are of course quite safe in the relatively small concentrations in which they are likely to be present in, for example, streams and rivers.

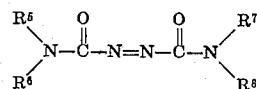
The compound azodicarbonamide itself has a low water solubility and so one cannot incorporate a sufficient amount in solution to give really rapid bleaching. Therefore, it is preferred to use one of its derivatives.

10 In copending and commonly owned U.S. Patent application Ser. No. 868,908 now U.S. Pat. No. 3,655,391, a number of azodicarbonamide derivatives for use as anti-fogging agents for photographic silver halide emulsions which generally have a higher water solubility than azodicarbonamide are described, and these derivatives can be used in the present invention. Reference is therefore made to that application for a full discussion and exemplification of these derivatives, and the disclosure of that application is hereby incorporated herein by reference. The preferred azodicarbonamide derivatives described in that application have the general formula:



25 30 in which R^1 to R^4 each individually are hydrogen or an alkyl, aryl, or heterocyclic group or pairs of groups $\text{R}^1 - \text{R}^2$ or $\text{R}^3 - \text{R}^4$, or both, represent atoms necessary to complete with the associated nitrogen atom a heterocyclic ring.

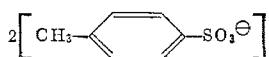
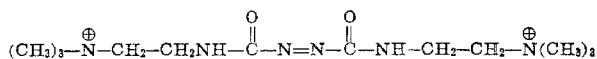
35 Other azodicarbonamides described in that application have the general formula:



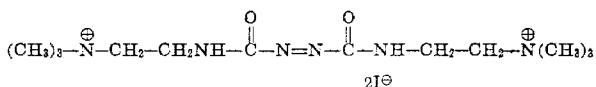
40 45 in which R^5 , R^6 , R^7 and R^8 may be hydrogen and wherein at least one of R^5 , R^6 , R^7 and R^8 represents alkoxalkyl, alkoxyaryl, hydroxy-alkyl, haloaryl, allyl, heterocyclic or heterocyclic-alkyl group.

50 55 For best results, however, we prefer to use the azodicarbonamide derivatives described in copending, commonly-owned U.S. Patent application Ser. No. 135,486 since the derivatives described in that application are highly soluble in water and so can be incorporated into a bleaching solution in large amounts to give a rapid bleaching action. Reference is, therefore, made to U.S. Patent application Ser. No. 135,486 for a full discussion and exemplification of those derivatives and the disclosure of that application is hereby incorporated by reference herein. The azodicarbonamide derivatives described in that application are those in which at least one of the amido nitrogen atoms has covalently bonded to it a group having a center of positive charge, e.g., a quaternary ammonium grouping, the derivative having associated with it at least one negatively charged moiety sufficient to impart electrical neutrality.

60 65 Examples of azodicarbonamide derivatives which we have found to work well are $\text{N},\text{N}'\text{-di}(\text{ethyl-2-trimethylammonium})\text{-azodicarbonamide di-toluene-p-sulphonate}$, i.e.,



and $\text{N},\text{N}'\text{-di(ethyl-2-trimethylammonium)azodicarbonamide di-iodide}$, i.e.,



although other azodicarbonamides described in the last mentioned U.S. Patent Application are also suitable.

The bleaching solution with which the developed silver is contacted will normally contain from a 0.01, and preferably a 0.03, molar amount up to a saturated solution, e.g., often about a molar solution, of an azodicarbonamide.

We find that we can accelerate the bleaching effect of azodicarbonamides by providing free halide ions in the bleaching solution. This can be readily achieved by incorporating a water-soluble halide such as potassium bromide in the bleaching solution.

Therefore according to another aspect of the invention there is provided a bleaching bath for bleaching a developed silver halide emulsion comprising an aqueous solution of an azodicarbonamide and a water-soluble halide, preferably a water-soluble bromide. We find that the bleaching effect of such a bleaching bath can be comparable with that of a ferricyanide bleaching bath. Desirably, the bleaching solution contains at least a 0.005 molar amount, and preferably from a 0.1 to 1.0 molar amount, of the water-soluble halide (preferably a bromide such as potassium bromide).

Frequently bleaching agents are used in combinations with a silver halide solvent so as to bleach and remove (fix) the resulting silver halide in a single step. This is called bleach-fixing. We have found that, provided the silver halide solvent is compatible with the azodicarbonamide which is employed (i.e., is non-reactive therewith) fixing can be effected at the same time as bleaching.

Therefore according to a further aspect of the invention there is provided a bleach-fixing bath for a developed silver halide emulsion comprising an aqueous solution of an azodicarbonamide, a compatible silver halide solvent, and preferably a source of halide (most preferably bromide) ions in the solution. This bleaching and fixing bath will generally contain at least a 0.1 molar amount of the silver halide solvent, and preferably from a 1.0 to 10 molar amount of the silver halide solvent. Such known silver halide solvents as sodium thiocyanate have been found suitable. Sodium thiosulphate is not suitable as the silver halide solvent because sodium thiosulphate will react with the azodicarbonamide and so destroy the latter's bleaching action. However, this can be turned to advantage when bleaching and fixing are not effected at the same time. Thus, if bleaching is first effected by the azodicarbonamide and fixing is thereafter effected by sodium thiosulphate, there is no need to wash the photographic material between the bleaching and fixing steps.

The azodicarbonamide bleaching agents of the invention are preferably used in bleaching developed silver at pH values of around 4 to 7, which is a common pH range for bleaching baths. Lower pH's generally favor faster bleaching. To keep the bleaching bath at desired pH values, a suitable buffer can be incorporated in the bleaching solution. Examples of suitable buffers are a sodium acetate/acetic acid combination, a potassium hydrogen phthalate and hydrochloric acid combination and a disodium hydrogen phosphate and citric acid combination.

The invention can be used in the bleaching of the developed silver from all types of photographic silver halide emulsions, e.g., those used in black and white and color films and the developed silver can be in one or more layers of a photographic emulsion. Also the grain size and chemical type of the silver halide emulsion does not appear to be critical.

The invention will now be illustrated by the following non-limiting Examples.

EXAMPLE 1

Azodicarbonamide was shaken in an aqueous solution of 1M KBr buffered to pH 4.97 at 20°C with 6 g of sodium acetate trihydrate and glacial acetic acid. Excess azodicarbonamide was filtered off. After 12 minutes in this solution a developed fine-grain emulsion showed a reduction in optical density from 2.36 to 2.00 as measured on a log scale, so representing a substantial reduction in silver. The silver salts were then removed from the emulsion by washing in a solution of sodium thiosulphate.

EXAMPLE 2

A bleaching bath was made up of the following composition: 150 ml of water, 3 g of $\text{N},\text{N}'\text{-di(ethyl-2-trimethylammonium) azodicarbonamide di-toluene-p-sulphonate}$, 3 g of KBr, and acetic acid to bring the pH to 4.0 at 21.5°C.

The rate of bleaching of developed silver in a fine-grain emulsion was measured by observing the change in density for various bleaching times. The average rate of bleaching over the first minute was 0.35 density units per minute. Between one minute and four minutes the density decreased at a constant rate of 0.12 density units per minute.

EXAMPLE 3

$\text{N},\text{N}'\text{-Di(ethyl-2-trimethylammonium) azodicarbonamide di-toluene-p-sulphonate}$ (3.16 g, 0.1M) was dissolved in a 1M aqueous KBr solution (50 ml). Sodium acetate trihydrate (3 g) was added and glacial acetic acid was added to a pH of 4.96 at 20°C. This solution was used to bleach developed silver from a developed X-ray photographic emulsion having an average grain diameter of about $1.5\text{ }\mu$. An initial density of 1.7 was reduced to 0.61 in 1 minute.

EXAMPLE 4

$\text{N},\text{N}'\text{-Di(ethyl-2-trimethylammonium) azodicarbonamide di-iodide}$ (2.84; 0.1M) was dissolved in 1M aqueous KBr solution (50 ml). Sodium acetate trihydrate (3 g) was added, and glacial acetic acid was added to a pH of 4.96 at 20°C.

This solution was used to bleach developed silver from a developed X-ray photographic emulsion having

an average grain diameter of 1.5μ . An initial density of 1.7 was reduced to 0.8 in one minute.

EXAMPLE 5

A bleaching bath was compounded as follows:

N,N'-di(ethyl-2-trimethylammonium)	38 g
azodicarbonamide di-toluene-p-sulphonate	
potassium bromate	38 g
sodium acetate trihydrate	38 g
acetic acid	to pH 5.0
water	to 600 ml

This bleaching bath was substituted for a conventional ferricyanide bleach in the processing of an exposed Ferrania DIA 28 color reversal film using the following processing baths and processing sequence.

First Developer

hydroquinone	3.0 g
Phenidone	0.48 g
Calgon	1.2 g
sodium sulphite, anhydrous	22.2 g
borax	3.0 g
potassium bromide	1.5 g
potassium thiocyanate	0.48 g
sodium hydroxide	0.48 g
water	to 600 ml.

Stop-Hardener

sodium acetate, anhydrous	18.0 g
sodium metabisulphite	3.0 g
potassium alum	18.0 g
sodium bisulphite	15.0 g
water	to 600 ml.

Color Developer

diethyl paraphenylenediamine sulphate	1.68 g
Calgon	1.2 g
sodium carbonate, anhydrous	39.0 g
sodium sulphite, anhydrous	1.5 g
potassium bromide	0.72 g
sodium hydroxide	0.6 g
hydroxylamine hydroxylamine hydrochloride	0.6 g
water	to 600 ml.

Fixer

sodium thiosulphate, anhydrous	75.0 g
water	to 600 ml.

The processing sequence was as follows:

First development	13 minutes
Wash	1 minute
Stop	5 minutes
Wash	5 minutes
Reversal exposure	11 minutes
Color development	1 minute
Wash	5 minutes
Stop	5 minutes
Wash	5 minutes
Bleach	10 minutes
Wash	5 minutes
Fix	5 minutes
Wash	15 minutes
Dry	

All processing was carried out at 20°C.

The resulting transparencies were comparable to those obtained when processed with a conventional ferricyanide bleach.

EXAMPLE 6

A bleach-fix solution was made up by the addition of 4.7 g of sodium thiocyanate to the bleaching bath described in Example 3. This solution was found to remove both developed silver and undeveloped silver halide from a photographic film.

EXAMPLE 7

A bleaching bath was prepared from 250 ml of water, 31.6 g (0.2M) of N,N'-di(ethyl-2-trimethylammonium) azodicarbonamide di-toluene-p-sulphonate, 12 g (0.4M) of KBr, 5 g of anhydrous sodium acetate and glacial acetic acid to bring the pH to 4.1.

Kodak Ectachrome-X color reversal film was exposed and then developed conventionally following standard Kodak E-4 processing (see, for example, The British Journal of Photography Annual 1972, page 209) with the exception that the bleaching bath of this example was used to bleach the silver from the film. Full bleaching of the silver was accomplished in 2 minutes at 20°C. When the resulting processed film was compared with an identical film processed following standard Kodak E-4 processing, no change in the color balance could be observed.

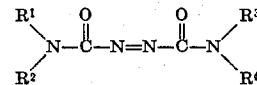
The stability of the above bleaching bath during storage in a stoppered bottle was checked over a period of four months. The bleaching efficiency was monitored periodically by measuring the rate of bleaching of developed silver from a fully developed X-ray photographic film. No change in bleaching properties was observed for the first two months of storage but after four months of storage the bleaching rate was found to have decreased slightly by about 10 percent of its initial rate. The bleaching bath can, therefore, be said to have good storage properties.

As can be seen from the above Examples, azodicarbonamides can be used in place of the highly toxic ferricyanide bleaching agents to bleach developed silver from an exposed and developed silver halide emulsion. Their use has, however, the important advantage that they are substantially non-toxic and so they can be used and disposed of without any special precautions. Additionally, azodicarbonamides decompose quite quickly in solution and so are not liable to build-up in concentration in rivers and streams.

What we claim is:

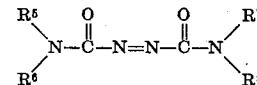
1. A process for bleaching photographically developed silver comprising contacting the developed silver with an aqueous processing solution containing, as a bleaching agent, an azodicarbonamide.

2. A process as claimed in claim 1 wherein said azodicarbonamide is of the formula:



in which R¹ to R⁴ each individually are hydrogen or an alkyl, aryl or heterocyclic group, or the pairs of groups R¹ - R² or R³ - R⁴, or both, represent atoms necessary to complete with the associated nitrogen atom a heterocyclic ring.

3. A process as claimed in claim 1 wherein said azodicarbonamide is of the formula:



in which R⁵ to R⁸ may be hydrogen and wherein at least one of R⁵, R⁶, R⁷ to R⁸ represents an alkoxyalkyl, alkoxaryl, hydroxyalkyl, haloaryl, allyl, heterocyclic or heterocyclic-alkyl group.

4. A process as claimed in claim 1 in which the solution contains at least one azodicarbonamide derivative in which at least one of the amido nitrogen atoms has covalently bonded to it a group having a center of positive charge, the derivative having associated with it at

least one negatively charged moiety sufficient to impart electrical neutrality.

5. A process as claimed in claim 4 in which the group having the center of positive charge is a quaternary ammonium grouping.

6. A process as claimed in claim 4 in which the solution contains N,N'-di(ethyl-2-trimethylammonium) azodicarbonamide di-toluene-p-sulphonate, and/or N,N'-di(ethyl-2-trimethylammonium) azodicarbonamide-di-iodide.

7. A process as claimed in claim 1 in which the solution contains from a 0.01 molar amount up to a saturated solution of said azodicarbonamide.

8. A process as claimed in claim 7 in which the solution contains from a 0.03 molar amount up to a saturated solution of said azodicarbonamide.

9. A process as claimed in claim 1 in which the solution additionally contains free halide ions.

10. A process as claimed in claim 9 in which the halide ions are bromide ions.

11. A process as claimed in claim 9 in which the solution contains a water soluble halide which provides the free halide ions in solution.

12. A process as claimed in claim 11 in which the solution contains at least a 0.005 molar amount of the water soluble halide.

13. A process as claimed in claim 12 in which the solution contains from 0.1 to 1.0 molar amount of the water soluble halide.

14. A process as claimed in claim 11 in which the water soluble halide is potassium bromide.

15. A process as claimed in claim 1 in which the solution has a pH of from 4 to 7.

16. A process as claimed in claim 15 in which the solution contains a buffer to maintain the desired pH.

17. A process as claimed in claim 16 in which the buffer is a sodium acetate/acetic acid combination.

18. A process as claimed in claim 1 in which said solution additionally contains a silver halide solvent compatible with said azodicarbonamide.

19. A process as claimed in claim 18 in which the solution contains at least 0.1 molar amount of the silver halide solvent.

20. A process as claimed in claim 19 in which the solution contains from a 1.0 to 10 molar amount of the silver halide solvent.

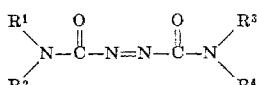
21. A process as claimed in claim 18 in which the silver halide solvent is sodium thiocyanate.

22. A process as claimed in claim 1 in which, after bleaching the developed silver from a developed photographic silver halide photographic emulsion, and without intermediate washing, the emulsion is thereafter fixed by contact with an aqueous solution of a silver halide solvent which reacts with said azodicarbonamide.

23. A process as claimed in claim 22 in which the silver halide solvent is sodium thiosulphate.

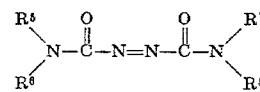
24. A bleaching bath for bleaching a developed silver halide photographic emulsion comprising an aqueous solution of an azodicarbonamide and a water soluble halide.

25. A bleaching bath as claimed in claim 24 which contains an azodicarbonamide derivative having the general formula:



in which R¹ to R⁴ each individually are hydrogen or an alkyl, aryl or heterocyclic group, or the pairs of groups R¹ - R² or R³ - R⁴, or both, represent atoms necessary to complete with the associated nitrogen atoms a heterocyclic ring.

26. A bleaching bath as claimed in claim 24 which contains an azodicarbonamide derivative having the general formula:



in which R⁵ to R⁸ may be hydrogen and wherein at least one of R⁵, R⁶, R⁷ and R⁸ represents an alkoxyalkyl, alkoxyaryl, hydroxyalkyl, haloaryl, allyl, heterocyclic or heterocyclic-alkyl group.

27. A bleaching bath as claimed in claim 24 which contains at least one azodicarbonamide derivative in which at least one of the amido nitrogen atoms has covalently bonded to it a group having a center of positive charge, the derivative having associated with it at least one negatively charged moiety sufficient to impart electrical neutrality.

28. A bleaching bath as claimed in claim 27 in which the group having the center of positive charge is a quaternary ammonium grouping.

29. A bleaching bath as claimed in claim 27 which contains N,N'-di(ethyl-2-trimethylammonium) azodicarbonamide di-toluene-p-sulphonate, and/or N,N'-di(ethyl-2-trimethylammonium) azodicarbonamide-di-iodide.

30. A bleaching bath as claimed in claim 24 which contains from a 0.01 molar amount up to a saturated solution of said azodicarbonamide.

31. A bleaching bath as claimed in claim 30 which contains from a 0.03 molar amount up to a saturated solution of said azodicarbonamide.

32. A bleaching bath as claimed in claim 4 in which the water soluble halide is a water soluble bromide.

33. A bleaching bath as claimed in claim 24 which contains at least 0.005 molar amount of the water soluble halide.

34. A bleaching bath as claimed in claim 36 which contains from 0.1 to 1.0 molar amount of the water soluble halide.

35. A bleaching bath as claimed in claim 24 in which the water soluble halide is potassium bromide.

36. A bleaching bath as claimed in claim 24 which has a pH of from 4 to 7.

37. A bleaching bath as claimed in claim 36 which contains a buffer to maintain the desired pH.

38. A bleaching bath as claimed in claim 37 in which the buffer is sodium acetate/acetic acid combination.

39. A bleaching bath as claimed in claim 24 which is a bleaching-fixing bath and additionally contains a compatible silver halide solvent.

40. A bleaching bath as claimed in claim 39 which contains at least 0.1 molar amount of the silver halide solvent.

41. A bleaching bath as claimed in claim 40 which contains from a 1.0 to 10 molar amount of the silver halide solvent.

42. A bleaching bath as claimed in claim 39 in which the silver halide solvent is sodium thiocyanate.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,772,018

DATED : November 13, 1973

INVENTOR(S) : Swan, David W. & Duffin, George F.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Claim 32, "as claimed in claim 4 in which" should read as -- as claimed in claim 24 in which --.

Signed and sealed this 1st day of July 1975.

(SEAL)

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks