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[54] **DESTRUCTION OF EDTA BY ALKALINE CHLORINATION**

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[58] **Field of Search** ..... 96/60 R, 60 BF; 210/42, 48, 50, 59, 62; 252/188

[56] **References Cited**

UNITED STATES PATENTS

3,594,157	7/1971	Hendrickson et al.	75/118 X
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[57] **ABSTRACT**

Waste photographic processing solutions which contain ethylenediaminetetraacetate (hereinafter EDTA), such as exhausted ammonium iron EDTA bleaching or bleach-fixing solutions, are chlorinated to destroy EDTA and thereby increase the biodegradability of the solution. Chlorination can be effected by introduction of chlorine gas or by the use of hypochlorite solution. Since EDTA and complexes thereof account for a large portion of the oxygen consuming material present in photographic processing effluent, a significant source of water pollution is substantially eliminated by this method.

7 Claims, No Drawings

DESTRUCTION OF EDTA BY ALKALINE CHLORINATION

This invention relates in general to the photographic art and in particular to the treatment of waste photographic processing solutions. More specifically, this invention relates to treating waste photographic processing solutions which contain EDTA complexes or free EDTA, such as exhausted ammonium ferric EDTA bleach solutions, to convert the residual EDTA to innocuous reaction products so as to reduce water pollution resulting from disposal of the waste solution.

Until recently one of the most common class of bleaches comprised alkali metal ferricyanides, especially potassium ferricyanide. Much research has been performed to define substitutes for these materials in view of the potentially relatively high toxicity of the ferrocyanide compounds which form the bulk of the waste discharged after bleaching in view of the reaction products formed by such waste upon exposure of same to sunlight in streams, etc. If waste processing solutions containing hexacyanoferrate ion (the products of ferricyanide bleaching) are discharged to the sewer without treatment, these ions are slowly oxidized in the presence of ultraviolet radiation to cyanide ions, which are probably the most toxic to fish and other aquatic life of any of the chemicals discharged from photographic processes. A valuable substitute for the ferricyanide bleaches which is well known to those skilled in the photographic art are the ferric EDTA complexes, for example ferric ammonium EDTA or tetrasodium EDTA which, while producing excellent bleaching effects, do not yield the potentially toxic ferrocyanides of earlier ferricyanide systems. Thus, the most commonly used bleaching agent is rapidly becoming ferric ammonium EDTA which avoids the potential toxicity problems of the ferricyanide and demonstrates excellent bleaching properties, but which has been found to result in the discharge of materials requiring high chemical oxygen demand.

It is therefore an object of the present invention to provide a ready and relatively simple means of lowering the chemical oxygen demand of waste photographic solutions which contain EDTA.

According to the invention described in U. S. Pat. Application Ser. No. 851,464 of Hendrickson et al, filed, Aug. 19, 1969, and issued July 20, 1971 as U.S. Pat. No. 3,594,157, alkaline chlorination of waste photographic solutions containing thiosulfate ion destroyed the thiosulfate ion and consequently reduced the oxygen demand of the solution. It has now been discovered that a similar treatment of solutions containing EDTA complexes, whether they include thiosulfate or not, results in destruction of EDTA thereby greatly decreasing the chemical oxygen demand of waste solutions containing such compounds by converting the EDTA complexes to innocuous oxidation products.

The method comprises chlorination of the solutions under alkaline conditions, preferably at a pH above about 10 and advantageously at a pH above about 11.5 and comprises treating waste photographic processing solutions containing EDTA complexes and free of thiosulfate ion (treatment of such solution having already been described in the aforementioned patent) by chlorination.

An exhausted or waste EDTA bleach solution is a relatively complex solution which may typically contain,

in addition to EDTA complexes and free EDTA, materials such as alkali metal sulfites, alkali metal carbonates, gelatin hardening agents, acids, halides, gelatin, etc. In some instances the bleach may contain developer and/or developer oxidation products which are present as a result of carry-in from the developer solution. Even more complicated waste solutions containing EDTA complexes and free EDTA may be formed when different effluents from the photographic processing system are combined together before disposal, e.g. combined bleach and fix and/or prehardener, stabilizer baths, etc, and it is intended by use of the term "waste photographic processing solution" to include all such compositions. Regardless of the exact make up of the waste photographic solution, as employed herein the term "EDTA complex" is intended to mean all compounds comprising such materials which may be present in the waste solution, e.g. ferric ammonium EDTA, tetrasodium EDTA, free EDTA, etc.

As previously indicated, the method of this invention is not limited to treatment of exhausted fixing solution but is applicable to any photographic processing solution or other effluent containing EDTA in any of its many complexed or free forms. Thus, it may be used on combined processing effluents as described above.

Alkaline chlorination of waste bleach solutions can be carried out using batch, semicontinuous or continuous techniques. A preferable procedure is to bubble chlorine gas into the solution while adding sodium hydroxide to the solution to maintain the desired alkaline pH. The amount of chlorine gas used will depend upon the concentration of EDTA in the solution, the efficiency of the contacting procedure utilized, the extent to which residual EDTA in the treated solution can be tolerated, and so forth. Thus, the amount of chlorine used may vary from as little as about 1 to as much as about 100 volumes of chlorine gas per volume of solution, and this amount of chlorine can be provided by any combination of flow rate and time which will permit adequate contact between the solution and the chlorine.

Instead of effecting chlorination by introducing chlorine gas into the waste processing solution similar, however, somewhat less efficient EDTA destruction can be accomplished by adding hypochlorite to the solution. Results are essentially the same since the introduction of chlorine gas into an alkaline solution results in the formation of hypochlorite, an example of the reaction being as follows:

$$Cl_2 + NaOH \longrightarrow NaOCl + HCl$$

An advantage in employing the hypochlorite solution is that it is less hazardous to use. However, the use of chlorine gas tends to give a faster and more efficient reaction with EDTA.

Whether chlorination is accomplished by the use of chlorine gas or by the use of hypochlorite solution, it is preferably carried out in accordance with this invention under alkaline conditions. The required alkaline pH is most easily provided by the addition of a strong base to the solution, e.g. sodium hydroxide or potassium hydroxide, but any other suitable means of maintaining an alkaline pH known to the art may be employed. The strong base is preferably added simultaneously with the addition of the chlorine. While the method is operable at any alkaline pH, it proceeds most rapidly and efficiently at a high pH. It is, thus, preferred

to carry out the chlorination with the solution at a pH of greater than 10 and more preferably of 11.5 or more. Chlorination may also be carried out at slightly acid pH, however, the efficiency of the reaction is reduced substantially.

The invention is further illustrated by the following examples of its practice:

EXAMPLE 1

Chlorine gas is supplied from a gas cylinder into 1 liter of a 1.56 M NH_4Fe·EDTA (90 ml/1) solution at a regulated flow rate of 0.6 liters per minute. The pH of the reacting solution is kept above 11.0 by periodic addition of concentrated (16N) sodium hydroxide solution. The EDTA, EDTA-complex and iron concentrations are measured at regular intervals. The iron precipitates as the hydroxide and is easily filtered or otherwise removed as a precipitate by filtration after about 30 minutes. Chemical Oxygen Demand (COD) drops from an initial value of 38,300 mg/1 to a final value after 2.0 hours of treatment of 13,000 mg/1 and all EDTA was destroyed as proven by analysis.

EXAMPLE 2

Treatment of a solution of Na_4 EDTA (50 g/1) results in complete destruction of EDTA after a period of about 90 minutes, paralleling the results obtained in Example 1.

Addition of large volumes of caustic initially rather than periodically throughout the evaluation does not speed up EDTA degradation, however, it does provide a secondary advantage in that nearly all of the iron hydroxide precipitate can be removed prior to chlorination, thus avoiding plugging of the sintered glass-dispersion tubes conventionally used to bubble the chlorine gas into the solution by the precipitate. Further, heating the solution prior to chlorinating, does not appear to speed up degradation of EDTA.

Following examples are a continuation of those reported above. Table I describes the compositions of the bleach-fix formulations tested. The procedures utilized were as follows:

A. GASEOUS CHLORINATION

Table II is a description of the experimental conditions under which the separate trials were run. In Experiments 3–10, 350 ml concentrated (16N) sodium hydroxide were added to 1-liter samples of bleach-fix initially. Iron precipitated as the hydroxide, and the resulting solution was filtered with the aid of Analytical Grade Celite. The supernatant was then chlorinated. Chlorine (gas), supplied from a gas cylinder at a regulated flow rate, was bubbled into the bleach-fix solution through a gas-dispersion tube. All pH adjustments during chlorination were made with concentrated (16N) sodium hydroxide added periodically in 50-ml volumes. Samples were taken at various time intervals and analyzed for EDTA (SLM 1255, EDTA reported as Na_4EDTA), the EDTA-complex (as Na_4EDTA), total soluble iron (SLM 1254), and in some cases COD (Chemical Oxygen Demand), (SLM 1128). The bleach-fix sample was titrated with a standard zinc solution to form the zinc complex with the excess EDTA. In some instances, chlorination was interrupted to filter the reacting solution because a precipitate, assumed to be sodium chloride, plugged the gas-dispersion tube. Some trials were run for shorter time periods than others, either because of sodium chloride precipitate plugging the sparger or the volution of chlorine gas. The reaction of chlorine with the bleach-fix is exothermic, and maximum temperatures were always approximately 100 C.

In Experiments 3–7, the initial solution was a fresh bleach-fix. In Experiments 8–10, the initial solution was a formulation simulating the overflow to a silver recovery cartridge in a conventional bleach-fix process. Because chlorination also results in silver recovery, with silver in the spent bleach-fix precipitating as silver sulfide, chlorination can be used as a tailing operation. The concentration of EDTA is higher in the spent bleach-fix. Formulas are given in Table I.

B. ADDITION OF SODIUM HYPOCHLORITE SOLUTION

Two experiments were run in which concentrated Sunny Sol (analyzed at 16% sodium hypochlorite) was added to a 100-ml volume of spent bleach-fix and stirred. Volumes of Sunny Sol added were 380 ml in Experiment 9 and 760 ml in Experiment 10. Although the temperature did rise upon the addition of Sunny Sol, it never reached 100 C as occurred in gaseous chlorination. No pH adjustments were made. All iron did not immediately precipitate as the hydroxide as it did in gaseous chlorination, although a large percentage did form a precipitate. Samples were taken initially; immediately after addition; and after 1 hour, 24 hours, and 48 hours. They were analyzed immediately for EDTA, the EDTA-complex, and total soluble iron.

The results for all of these Examples are shown in Table III.

TABLE I

FORMULATIONS OF SOLUTIONS CHLORINATED

Fresh Bleach-Fix:

FeEDTA	91 ml/l
60% $(NH_4)_2S_2O_3$	125 ml/l
Na_2SO_3	12 g/l

Spent Bleach-Fix to Silver Recovery Cartridge:

FeEDTA	134 ml/l
60% $(NH_4)_2S_2O_3$	110 ml/l
Na_2SO_3	5 g/l

TABLE II.—Experimental Conditions of Gaseous Chlorination of Ektaprint 3 Bleach-fix

Example	Solution treated	Initial concentration of Na EDTA (g/1)	pH 11 maintained	Cl_2 (gas) flow rate l/min	Temperature of solution before chlorination	Initial volume (ml)
3.....	Fresh bleach-fix.	60	X	0.6	Room temp.	1,000
4.....	Fresh bleach-fix.	60	X	.6	Room temp.	900
5.....	Fresh bleach-fix.	55	X	.6	64° C.....	1,000
6.....	Fresh bleach-fix.	55	.....	.6	62° C.....	1,000
7.....	Bleach-fix overflow.	85	X	.6	Room temp.	970
8.....	Bleach-fix overflow.	85	X	1.2	Room temp.	970
9.....	Bleach-fix overflow.	176	X	.6	Room temp.	970

TABLE III

GASEOUS CHLORINATION — COD REDUCTIONS

Example 3		
Sample	COD (mg/l)	Overall Reduction = 99%
After Filter	60,000	
30 min	13,238	
60 min	9,265	
90 min	885	
120 min	500	
150 min	385	
Example 4		
Sample	COD (mg/l)	Overall Reduction = 99%
After Filter	58,100	
30 min	35,200	
60 min	20,000	
90 min	4,600	
120 min	2,800	
150 min	1,450	
180 min	760	
Example 5		
Sample	COD (mg/l)	Overall Reduction = 86%
After Filter	61,500	
30 min	47,100	
60 min	26,700	
90 min	8,800	
Example 6		
Sample	COD (mg/l)	Overall Reduction = 84%
After Filter	59,650	
30 min	54,950	
60 min	41,300	
90 min	9,550	
Example 7		
Sample	COD (mg/l)	Overall Reduction = 88%
After Filter	66,932	
30 min	54,177	
60 min	31,152	
90 min	8,645 Example 8	
Sample	COD (mg/l)	Overall Reduction = 88%
After Filter	61,250	
30 min	28,541	
60 min	7,381	
Example 9		
Sample	COD (mg/l)	
After Filter	—	
30 min	44,960	
60 min	49,344	
90 min	25,215	

It should be noted, however, that the amount of chlorine or hypochlorite utilized to achieve chlorination of EDTA will vary considerably depending upon the make up of the particular waste photographic solution being treated since many other materials present in such compositions may tend to utilize the chlorine in preference to the EDTA and therefore require the addition of significantly more chlorine.

As also demonstrated from the foregoing Examples, if the EDTA containing solution also happens to have iron, a compound alluded to as a polluter in some circles, present therein, as in the case of a major portion of the newest bleach materials which contain ferric ammonium EDTA, this compound is precipitated and easily removed from the effluent by filtration for safe disposal elsewhere.

The invention has been described in detail with particular reference to preferred embodiments thereof; however, it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A method of treating a waste photographic processing solution containing an iron complex of EDTA to reduce the oxygen demand of said solution so as to minimize water pollution resulting from disposal thereof, said method comprising the step of chlorinating said solution under alkaline conditions to destroy EDTA.

2. The method of claim **1** wherein said chlorination is carried out with said solution at a pH of greater than 10.

3. The method as described in claim **1** wherein said chlorination is carried out with said solution at a pH of about 11.5.

4. The method described in claim **1** wherein said chlorination is effected by introducing chlorine gas into said solution.

5. The method as described in claim **1** wherein said chlorination is effected by mixing said solution with hypochlorite solution.

6. A method for treating an exhausted ferric ammonium EDTA bleaching solution to precipitate iron therefrom and to reduce its oxygen demand so as to minimize water pollution resulting from disposal thereof, said method comprising the steps of

a. introducing sodium hydroxide into said solution to precipitate iron hydroxide which can be separated and

b. introducing a member selected from the group consisting of chlorine and hypochlorite into said solution to destroy EDTA.

7. The method of claim **6** wherein said steps (a) and (b) are performed simultaneously.

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