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**Stability of the Chlorinating Solution  
used in the Sawtri Chlorination Process**

by

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# STABILITY OF THE CHLORINATING SOLUTION USED IN THE SAWTRI CHLORINATION PROCESS

by E.C. HANEKOM and F.A. BARKHUYSEN

## ABSTRACT

*Relatively stable concentrated DCCA solutions with a low pH value were obtained by using a mixture of an organic and an inorganic acid. Different organic or combinations thereof with inorganic acids can be used to adjust the pH of the chlorination solution and to prevent or retard the precipitation of the DCCA from the solution.*

## KEY WORDS

DCCA — pH — precipitation — acetic acid — sulphuric acid — organic acid — inorganic acid — storage time — active chlorine content.

## INTRODUCTION

The use of alkali salts of DCCA (Dichloroisocyanuric acid) for the shrink-resist treatment of wool was advocated more than ten years ago. Mertens<sup>(1,2)</sup> hailed the alkali salts of DCCA for the ease and effectiveness which their employment allowed the rate of chlorination to be controlled.

Veldsman and Swanepoel<sup>(3)</sup> also investigated the rate of chlorination on the shrinkresist treatment of wool with DCCA and came to the conclusion that the pH of the chlorination solution is the most important factor which influences the rate of chlorination.

The rate of chlorination normally increases as the pH of the DCCA solution is decreased. For the most effective chlorination of wool on a continuous system, solutions containing relatively high concentrations of DCCA at a low pH value are normally required.

Until recently it was not possible to prepare stable concentrated solutions of DCCA at low pH values due to the precipitation of DCCA. By using a mixture of a suitable organic and inorganic acid or a suitable organic acid, however, solutions containing relatively high concentrations of DCCA were obtained at low pH values<sup>(4)</sup>. These solutions are stable for a time long enough to allow the continuous chlorination treatment of wool.

The purpose of this report is to indicate under which conditions relatively stable concentrated chlorination solutions can be prepared.

## EXPERIMENTAL

All experiments were carried out at room temperature. In all cases a mixture of an organic acid (glacial acetic acid) and an inorganic acid (sulphuric acid) was used, unless indicated otherwise. The concentration of the organic acid was 10 *per cent* (mass/volume) and that of the inorganic acid was approximately one *per cent* (mass/volume) of an 18 N sulphuric acid solution. In some cases where different inorganic acids were used to adjust the pH of the chlorination solution to 2, the amount of inorganic acid added depended on the particular acid used.

The potassium salt of DCCA, Basolan DC (BASF), was dissolved in water and 0,5 *per cent* wetting agent Tergitol Speedwet, (Union Carbide) was added to this solution. The organic acid (glacial acetic acid) was then added followed by the inorganic acid (sulphuric acid) to adjust the pH to the desired value. These acids can also be added as a mixture to the DCCA solution. In all cases solutions containing 1,5 *per cent* active chlorine were used in the experiments.

For the determination of the active chlorine content of the solutions an aliquot of five ml was taken from 100 ml prepared solution and diluted to 250 ml with distilled water. Potassium iodide and sulphuric acid were added to 25 ml of this solution. The liberated iodine was then titrated against 0,1 N sodium thiosulphate. An accurate end point was obtained by means of a starch indicator. The active chlorine content was determined by means of the following formula:

$$\% \text{ Active chlorine} = \text{ml thiosulphate} \times \text{Normality of thiosulphate} \times 0,0355 \times 200 \quad (1,0 \text{ ml } 1 \text{ N thiosulphate} = 0,0355 \text{ g available chlorine}).$$

To establish the percentage loss of active chlorine in solutions where precipitation occurred, the solution was filtered through filter paper and an aliquot was then taken from the filtrate for the determination of the active chlorine content as described above.

The following parameters were investigated:

- (a) Effect of time and concentration of acetic acid on the percentage active chlorine in solution.
- (b) Effect of other organic acids as substitutes for acetic acid.
- (c) Effect of different combinations of organic and inorganic acids.
- (d) Solubility of DCCA precipitate in different concentrations of various organic acids.
- (e) Effect of pH on the stability of chlorination solutions.

The DCCA was obtained by dissolving Basolan DC in water and lowering the pH with sulphuric acid. The precipitated DCCA was then filtered off, washed with water and dried.

**TABLE I**

**THE EFFECT OF TIME OF STORAGE ON THE PERCENTAGE ACTIVE CHLORINE IN ACETIC ACID SOLUTIONS OF DIFFERENT CONCENTRATIONS AT A PH OF 2\***

TIME (mins.)	% ACTIVE CHLORINE			
	0% CH <sub>3</sub> COOH	10% CH <sub>3</sub> COOH	15% CH <sub>3</sub> COOH	20% CH <sub>3</sub> COOH
0	—	1,49	1,42	1,49
75	—	1,28	—	—
100	—	1,28	—	—
150	—	1,21	—	—
170	—	0,92	—	—
190	—	0,85	—	—
210	—	0,78	—	—
225	—	0,71	—	—
270	—	0,56	1,14	—
1 260	—	0,64	0,71	0,78

\* An 18 N H<sub>2</sub>SO<sub>4</sub> solution was used in all cases to obtain a pH of 2.

**RESULTS AND DISCUSSION**

Throughout this discussion the amount of active chlorine in the solution was taken as a measure of the stability of the chlorinating solution. The organic acids used in the tests were acids which are not readily chlorinated or oxidised. Tergitol Speedwet, was used as the wetting agent in all the experiments.

- (a) Effect of time and concentration of acetic acid on the percentage active chlorine in solution.

From the results in Table I it is clear that with no acetic acid present in the solution i.e. the pH adjusted to 2 with H<sub>2</sub>SO<sub>4</sub> only, excessive precipitation of DCCA occurred and therefore no active chlorine values were determined. In the presence of acetic acid the solution was, however, fairly stable. In the presence of 10 *per cent* acetic acid the loss in active chlorine was 14,1 *per cent* after 75 minutes and 62,4 *per cent* after 270 minutes. With 15 *per cent* acetic acid a much more stable solution was obtained since the loss in active chlorine after 270 minutes was only 19,7 *per cent*.

From Table I it can, therefore, clearly be seen that an increase in the concentration of the acetic acid resulted in a more stable chlorination solution. It should, therefore, be clear that a suitable organic acid such as acetic acid is a prerequisite for stabilising the DCCA solution at pH of 2,0 or even lower.

**(b) Effect of other organic acids as substitutes for acetic acid.**

From the results of Table II it can be concluded that DCCA solutions can also be stabilized by the use of halogenated acetic acids.

**TABLE II**

**THE EFFECT OF DIFFERENT ORGANIC ACIDS AND STORAGE TIME ON THE ACTIVE CHLORINE CONTENT OF A DCCA SOLUTION AT pH 2,0**

TIME (mins.)	% ACTIVE CHLORINE			
	CH <sub>3</sub> COOH	CH <sub>2</sub> ClCOOH	CCl <sub>2</sub> COOH*	CF <sub>3</sub> COOH*
0	1,56	1,56	1,49	1,49
1	1,56	1,42	1,49	1,42
2	1,56	1,49	1,42	1,42
3	1,56	1,56	1,49	1,42
4	1,56	1,42	1,49	1,42
5	1,56	1,49	1,42	1,42
10	1,49	1,42	1,49	1,42
20	1,56	1,42	1,49	1,20

\* No sulphuric acid was necessary in these cases to obtain the desired pH value. Concentration of these acids to achieve a pH of 2,0 were:  
 1,92% Dichloroacetic Acid (mass/volume)  
 2,20% Trifluoroacetic Acid (mass/volume)

The times taken for these solutions to become milky (i.e. for precipitation to start) were:

Acetic Acid	:	About 30 mins
Monochloroacetic Acid	:	Immediately
Dichloroacetic Acid	:	About 45 mins
Trifluoroacetic Acid	:	About 17 mins

With the possible exception of trifluoroacetic acid no significant differences in the active chlorine values were obtained by using the halogenated acetic acids (Table II) for periods up to 20 minutes.

**TABLE III**

**THE EFFECT OF DIFFERENT COMBINATIONS OF SUITABLE ORGANIC (10%, m/v) AND INORGANIC ACIDS ON THE ACTIVE CHLORINE CONTENT OF A CHLORINATING SOLUTION AT pH 2,0**

SOLUTION	I	II	III	IV	V	VI
TIME (mins.)	CH <sub>3</sub> COOH+ 1,25% HC1	CH <sub>3</sub> COOH+ 2,1% HNO <sub>3</sub>	CH <sub>3</sub> COOH+ 2,6% H <sub>3</sub> PO <sub>4</sub>	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> *+ 1,25% HC1	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> *+ 1% HNO <sub>3</sub>	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> *+ 2,8% H <sub>3</sub> PO <sub>4</sub>
0	1,49	1,49	1,49	1,35	1,56	1,49
1	1,56	1,49	1,45	1,42	1,49	1,42
2	1,42	1,45	1,49	1,42	1,56	1,42
3	1,56	1,45	1,42	1,38	1,52	1,42
4	1,42	1,49	1,49	1,42	1,52	1,35
5	1,45	1,45	1,42	1,38	1,56	1,45
10	1,42	1,45	1,42	1,42	1,56	1,45
20	1,35	1,45	1,35	1,35	1,56	1,49
Precipitation starts approximately after:	12 mins	30 mins	25 mins	5 mins	20 mins	Immediately

\* Propionic acid

Washing test results of knitted samples, made from wool tops chlorinated with the solutions given in Table II and subsequently resin treated with an aminoplast resin were excellent <sup>(5)</sup>.

**(c) Effect of different combinations of suitable organic and inorganic acids.**

From Table III it will be observed that as far as the active chlorine content of the solution is concerned any of the above combinations of acids can be used. From the times these solutions stood before precipitation started (i.e. until the first sign of precipitation was noticed), it can be seen that the active chlorine content of the solutions did not decrease significantly, despite the fact that precipitation started fairly soon in the case of some of the solutions. In the case of solution IV, for example, precipitation started after 5 minutes whereas in solution VI precipitation started immediately on the addition of the inorganic acid and yet the active chlorine contents of these solutions were still virtually unchanged after standing for 20 minutes. These results, therefore, show that a noticeable precipitation of the chlorination solution does not necessarily mean a significant loss of the percentage active chlorine of that particular solution.

**(d) Effect of different combinations of organic and inorganic acids**

The results in Table IV illustrate that an increase in the organic acid

**TABLE IV**

**THE SOLUBILITY OF DCCA IN DIFFERENT CONCENTRATIONS OF ACETIC AND PROPIONIC ACID (vol./vol.)**

ACID	MASS OF DCCA DISSOLVED (GRAMS)					
	0% Acid	10% Acid	20% Acid	30% Acid	40% Acid	50% Acid
CH <sub>3</sub> COOH	1,3	2,0	2,45	2,6	2,4	3,05
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	1,1	1,4	1,8	2,1	2,8	3,2



TABLE V

A COMPARISON OF THE STABILITY OF CHLORINATION SOLUTIONS (1,5% ACTIVE CHLORINE) WITH AND WITHOUT ACETIC ACID AT DIFFERENT pH VALUES

pH	TIME (MINS.) BEFORE PRECIPITATION STARTED		
	0% CH <sub>3</sub> COOH	10% CH <sub>3</sub> COOH	20%* CH <sub>3</sub> COOH
3,0	Immediately	101	900
2,5	—	70	—
2,0	—	35	—
1,5	—	16,5	—
1,0	—	16,5	120

\* The pH of the 20% CH<sub>3</sub>COOH solution was 3,0; addition of H<sub>2</sub>SO<sub>4</sub> to this solution was, therefore, not necessary.

In all other cases H<sub>2</sub>SO<sub>4</sub> was used to adjust the pH of the solution to the required value:

concentration increases the solubility of DCCA. It can therefore be concluded that the organic acid not only acts as a hydrogen ion donor, but also as a solubilizing agent for the DCCA which is formed during the process, thereby retarding its precipitation.

(e) Effect of pH on the stability of chlorination solutions.

From Table V it is obvious that precipitation already occurred at a pH value of 3,0 in the absence of acetic acid. In the presence of acetic acid, however, relatively stable solutions were obtained. The stability of the solutions decreased with a decrease in the pH value.

With 20 per cent acetic acid, however, precipitation started only after the solution had been standing for approximately 15 hours at pH 3,0, and for about 2 hours at pH 1,0. The stability of the solution, therefore, can be improved by an increase in the concentration of the acetic acid.

It must be emphasized that all investigations were carried out in a laboratory. In actual practice, however, when wool is padded with a chlorination solution, the time before precipitation starts, the active chlorine content of the solution may differ from that obtained in the laboratory. With adequate apparatus such as metering pumps, where the acid mixture and DCCA-solution are mixed just before being used, no problems should be encountered during the chlorination process. Approximately 1 000 kg of wool tops were chlorinated at a textile mill according to the method used in the laboratory. Under these conditions it was found that no precipitation of DCCA at pH 2,0 occurred for periods of up to 90 minutes.

### SUMMARY AND CONCLUSIONS

From the results obtained it is concluded that the use of a suitable organic acid is a prerequisite for stabilising a DCCA chlorinating solution at relatively low pH values. From the results obtained in laboratory experiments as well as for economical reasons at least 10 *per cent* of a suitable organic acid, such as glacial acetic acid, is preferred for stabilising the chlorination solution especially at low pH values. When no suitable organic acid is present in the solution, precipitation of the chlorination reagent started almost immediately, even at relatively high pH values, resulting in a considerable decrease of the available active chlorine in the solution. The stability of the DCCA solutions increased when the concentrations of suitable organic acids, such as acetic acid or halogenated acetic acids, were increased. Certain halogenated acetic acids can be employed to obtain the desired low pH value without having to add an inorganic acid. Furthermore, different combinations of various suitable organic and inorganic acids can be used to produce stable DCCA solutions at a relatively low pH value.

The most important observation to be made from the results is the fact that without a suitable organic acid in the presence of an inorganic acid it is impossible to obtain a sufficiently stable concentrated solution of DCCA at relatively low pH values. It was found that the organic acid used acts as a hydrogen ion donor as well as a solubilizing agent for DCCA, which is formed in the chlorination solution, thereby retarding the precipitation of the DCCA.

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## THE USE OF PROPRIETARY NAMES

The use of proprietary names in this report by no way implies that they are recommended and that there are not substitutes which have the same or even better properties.

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