

A New Method for the Preparation of Copper Oxychloride (A Fungicide)

MUHAMMAD ISHAQUE QAIMKHANI*, RASHID ALI SIDDIQUI, MUHAMMAD RAUF
AND SHAHNAZ PARVEEN

PCSIR Laboratories Complex, Karachi-75280, Pakistan.

(Received 7th February 2006, revised 23rd July 2007)

Summary Copper oxychloride $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ has been prepared by the aeration of copper in acidic (HCl) solution of sodium chloride (NaCl). The results were compared with those of two other similar methods; one is involved with aeration of copper in acidic (HCl) solution and in the other copper was aerated in sodium chloride solution. The results showed that the reaction in the newly developed method is faster than the reaction of the latter two.

Introduction

It has universally been accepted that fungicides have become indispensable for protecting crops and plants from damage and destruction that is caused by fungi. Copper based fungicides were among the first crop protection chemicals to be used and are still used very extensively [1]. Copper sulfate (CuSO_4) was the first chemical to be used as seed treatment to control the bunt of wheat. Although CuSO_4 is an excellent fungicide in its own right but it is little used on plant foliage because of its high degree of phytotoxicity [2]. Then the Bordeaux mixture became the most popular fungicide to control dewing mildew of grapes and several other plant diseases [3]. The development of 'fixed' or "insoluble" copper compounds, which are generally considered to be less phytotoxic than Bordeaux mixture, began about 1930 and was undoubtedly accelerated by constant evidence showing that various crops were injured more than previously realized by the application of Bordeaux mixture [2]. The most important and widely used fixed copper compound is copper oxychloride, $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$, which is also called basic cupric chloride, generally recommended for control of a variety of vegetable diseases. It is toxic to the fungi and non toxic to host plants and has low mammalian toxicity. It is also used as fungicidal pigment in paints and as wood preservative when incorporated in concrete used for flooring. It destroys fungi, molds and bacteria and is used to draw away cockroaches, especially in warm humid countries where these organisms as well as insects are troublesome [4]. Copper oxychloride has been produced by various methods:

1. Electrolysis of Brine at a copper-anode and by the controlled neutralization of cupric oxide with hydrochloric acid in water [2].

2. Reacting cupric chloride in solution with cupric hydroxide [4].
3. Neutralizing copper hydroxide in solution with hydrochloric acid [4].
4. Oxidization of cuprous chloride in air to basic chloride [4].
5. Reacting cupric chloride with calcium carbonate in water [5].
6. Treating cupric chloride with sodium hydroxide solution [6].

Almost all of these methods involve costly copper compounds as basic raw material, which ultimately affect the finished cost of this chemical. It was therefore, decided to produce copper oxychloride from cheap copper scrap as a starting material. A few references about the two methods *viz.* aeration of copper in sodium chloride solution [2, 7] and aeration of copper in hydrochloric acid [8, 9] are available in literature. A third method has been evolved by these authors by combining certain points of the two methods, and it has been found to be superior to the two former methods under similar operative/ processing conditions.

Results and Discussion

Three methods have been tried for the production of copper oxychloride. The following Table shows the comparison of the results of these methods.

NaCl, HCl separately and mixture of the two have been tried as a source of chloride for the production of copper oxychloride in methods I, II and III respectively. Results of method-I show that no appreciable reaction occurred, as almost all copper

*To whom all correspondence should be addressed.

Table-1: Comparison of Three Methods.

Quality of reactants and reaction observations	Method-I	Method-II	Method-III
1. Copper metal (wire) 95.5 % Size length-1 mm. diameter 0.315 mm.	50 gm.	50 gm.	50 gm.
2. Actual copper present.	47.75 gm	47.75 gm	47.75 gm
3. Hydrochloric Acid Purity 37 %.	--	350 ml	350 ml
4. Sodium Chloride Purity 99 %.	150 gm	--	150 gm
5. Time duration of Reaction.	30 hrs	30 hrs	30 hrs
6. Unconsumed copper after 30 hrs aeration.	47 gm	5 gm	Nil
7. Color of solution before aeration	Colorless	Colorless	Colorless
8. Color of solution after aeration.	Colorless	Dark green	Dark green
9. pH of solution before aeration.	7 (Neutral)	1-2 (Acidic)	1-2 (Acidic)
10. pH of solution after aeration.	7 (Neutral)	4-5 (Acidic)	4-5 (Acidic)
11. Copper Oxychloride Produced.	Nil	69.5 gm	78.2 gm
12. Temperature of the reaction.	90-100C°	90-100C°	90-100C°
13. Rate of aeration (airflow).	0.33 L/ min	0.33 L/ min	0.33 L/ min
14. Theoretical yield.	--	71.86 gm	80.27 gm

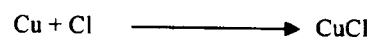
remained unconsumed after 30 hrs aeration. A very small white coating was seen on copper pieces. Solution in method-I remained colorless and neutral even after aeration, which also indicates that no reaction had taken place in this method.

Results of methods II and III show that a substantial quantity of copper oxychloride has been produced in both. Comparison of the results of method II and III reveals, that the reactions in method III are faster than that in method II, as in the reaction time 30 hours all the copper has been consumed in method III, 5 gm. copper still remained unconsumed in method II. On the other hand in the same time 80.27 gm copper oxychloride has been produced in method III, where as only 71.86 gm copper oxychloride has been produced in method II. Optimization of method II, required further 3-hours.

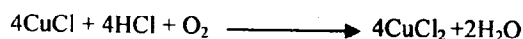
Reactions in Newly Developed Method (III)

The possible reactions in method III, also supported by literature are as follows:

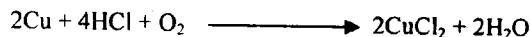
Copper reacts with chloride (from NaCl solution) to form insoluble cuprous chloride (CuCl) [10] which is highly soluble in hydrochloric acid [4].



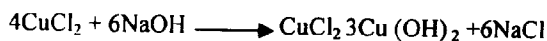
Cuprous chloride, when aerated in acidic conditions, forms cupric chloride (CuCl₂) [10-12].



Simultaneously hydrochloric acid acts on copper in the presence of oxygen in air and copper gradually dissolves according to the equation [13].

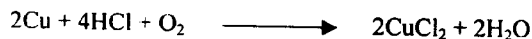


Dark green acidic solution of cupric chloride formed as a result of aeration, when neutralized with sodium hydroxide (NaOH), produces copper oxychloride [6].

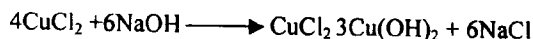


Reactions in Method II

Hydrochloric acid acted on copper in presence of oxygen and copper gradually dissolved according to the equation [13]



Cupric chloride (CuCl₂) so formed, when neutralized with sodium hydroxide solution produces copper oxychloride [6].



Reaction in Method I

Copper when immersed in chloride solution becomes coated with almost insoluble cuprous chloride [10].



This insoluble coating prevents the copper from further reaction.

Reasons for no Further Reaction in Method I as Compared to the Reactions in Methods II and III.

As mentioned above, in case of method II, hydrochloric acid reacts with copper in presence of oxygen and cupric chloride was formed. This cupric chloride then reacts with sodium hydroxide to form copper oxychloride and there was no hindrance in further proceeding of the reaction. In methods I and III, the first step is formation of cuprous chloride. Oxidation of cuprous chloride to cupric chloride by air depends on its solubility in the media. In case of method III, the medium is hydrochloric acid, in which cuprous chloride is very soluble and effective absorbent for oxygen [2, 4, 14], so further reactions proceeded smoothly. In case of method I, the medium of oxidation was sodium chloride solution. The literature shows contradiction about the solubility of cuprous chloride (CuCl) in this solution. e.g CuCl is soluble in water in presence of sodium chloride (NaCl) [7]. CuCl in conc. NaCl oxidized with O₂ in presence of dispersing agent [15]. Solubility of CuCl increases with increase in temperature and decreases with increasing concentration of NaCl [16]. CuCl precipitates if small amount of chloride ion is present [17]. Sufficient alkali metal chloride (NaCl) is required to retain CuCl in solution [18]. Copper when immersed in chloride solution becomes coated with almost insoluble CuCl [10].

Under existing operative and processing conditions in method I, the copper pieces coated with insoluble CuCl. This on one hand prevented the copper to react further with chloride to form more CuCl and on the other hand so formed insoluble CuCl could not oxidize to CuCl₂. Hence no further reaction takes place with the result that no copper oxychloride is formed.

Reasons for Faster Rate of Reactions in Method III as Compared to the Reactions in Method II.

As far as the formation of copper oxychloride via CuCl₂ by the action of HCl on copper in presence of oxygen [13] is concerned, both the methods are similar, but in case of method III, there is also another extra route for the formation of copper oxychloride i.e., via cuprous chloride. So the time for

total consumption of copper in method III is lesser than that in case of method II i.e., overall reactions in method III are faster than those in case of method II.

Experimental

Three solutions, as mentioned below, were prepared for use in the three methods from analytical grade chemicals and distilled water.

1. 150 gm NaCl in 300 ml H₂O method-I
2. 350 ml HCl (12 N) in 300 ml H₂O method-II
3. 150 gm NaCl in 350 ml HCl (12 N) in 300 ml H₂O... method-III

To each solution was added 50gm equal sized washed and dried copper wire (length 1-mm dia 0.315-mm), and then the solutions were separately aerated at the same rate (0.33 L/ min) and temperature (90-100 C°), till copper in either of the three solutions was completely consumed. Solution (1) was still colourless and neutral as no reaction took place in this solution except only small white coating was seen on copper pieces, so no further action was carried out with this solution. Solutions (2) and (3) were strongly acidic and their colour changed from colourless to dark green during aeration. These two solutions were filtered and neutralized with sodium hydroxide solution. Green precipitate, so formed, was filtered, washed, dried and analyzed for copper oxychloride. Copper and chloride contents in copper oxychloride were estimated titrimetrically [19]. After 30 hrs aeration all the copper in solution (3) had been consumed, where as 5 gm copper remained unconsumed in solution (2), which in a separate set of reaction required further 3 hours aeration for complete consumption of the copper.

References

1. D. S. Hill and J. M. Waller, *Pest and Diseases to Tropical Crop* Intermediate tropical Agriculture series longman London 1, 142 (1974).
2. Allison Butts, *Copper*, Reinhold Publishing Corporation New York 795, 813, 816, 818 (1960).
3. K. C. Gupta, R. A. Singh and B. Das, *Pesticide XIV* 29 (1980).
4. Kirk Othmer, *Encyclopedia of Chemical Technology*, 2nd Edn., Inter science publishers New York, 6, 271 (1963).

5. A. V. Shikarev, Agal't sov, A. M. (Pervamaisk P. O. Khimprom, Pervomisk (USSR) Khim Tekhnol (Kiev) 1990 (2) 50-2 (Russ). C. A. 112, 237646 (1990).
6. E. D. Witman Swiss Patent 2, 4, 3,271 (1946). C. A. 44, 1658 (1950).
7. Chemical Technology. An Encyclopedic Treatment Barnes and Noble Inc. Publishers New York, 1, 566 (1968).
8. Kendals Hall, Rodlett and Herrts, *Copper Compounds in Agriculture and Industrial Microbiology*, Copper Development Association England, 27 (1948).
9. M. B. Green, G. S. Hartley and T. F. West, *Chemical of Crop Protection and Pest Control*, Pergamon Press Oxford New York, 106 (1979).
10. C. A. Jacobson, *Encyclopedia of Chemical Reaction*, Reinhold publishing Corporation III, 287, 319 (1949)
11. A. S. Jhaveri and M. M. Sharma, *Chemical Engineering Science*, 22, 1 (1976).
12. Knapsack-Grieskeim, Akt-Ges German Patent 1, 014, 973 (1957). C. A. 53 22784 (1959)
13. G. Brooks King and William E. Caldwell *The Fundamentals of College Chemistry* 2nd Edn., American Book Co. New York 451 (1954).
14. E. de Barry Barnett and G. L. Wilson *Inorganic Chemistry* 2nd Edn., 257 (1962).
15. Heinz Pohlemann, Haiez Applex and Karl Jackel German Patent 1044789 (1958). .A. 54 25633 (1960).
16. G. N. Sin, I. N. Shokin and A. G. Kuznetsova., *Tr. Mosk. Khim Tekhnol Inst.*, No. 47, 111 (1964) (Russ). C.A. 64 10462 (1966).
17. Leo Patrick Curtin, *Ind. Engg. Chemistry*, 19, 993 (1927).
18. Pierre F. J. Souviron, Pierre E. Bigourdan and Bul Bebin, British Patent; 425325 (1935) C. A. 29, 5608 (1935).
19. I. Vogel, *Quantitative Inorganic Analysis* 3rd Edn., The English Language Book Society & Longmans green & Co. Ltd., 260 (1961).