

## THE ACTION OF CARBON DIOXIDE ON BORDEAUX MIXTURES.

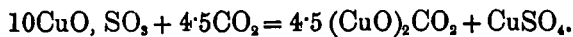
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THE fungicidal properties of the insoluble copper compounds, present in Bordeaux mixtures, have long been known, and it is an important point to ascertain the precise manner in which the poisonous action is exerted. A variety of theories have been put forward, but the matter cannot be regarded as settled. It has been generally accepted that, in order to account for the fungicidal action, it is necessary to look for some means by which the insoluble copper in Bordeaux mixture is rendered soluble when the material is sprayed on to foliage. Atmospheric carbon dioxide has frequently been suggested as the most important agent by which this is effected, and recently this view has been urged by Mr S. U. Pickering, F.R.S., who has also investigated in detail, the chemical nature of the compounds found in Bordeaux mixtures.

Pickering showed<sup>1</sup> that the addition of lime, in gradually increasing amounts, to solutions of copper sulphate, resulted in the formation of a series of basic sulphates of copper. The final compound present in ordinary Bordeaux mixture (*i.e.* made from equal weights of lime and copper sulphate) is  $10\text{CuO}, \text{SO}_3, 3\text{CaO}$  in presence of large excess of free lime; in Bordeaux mixtures made without excess of lime, it is either  $4\text{CuO}, \text{SO}_3$ ,  $5\text{CuO}, \text{SO}_3$  or  $10\text{CuO}, \text{SO}_3$ , depending on the proportion of lime-water added, the latter being the compound employed in making Woburn Bordeaux Paste.

Pickering then states his opinion that when any of these basic sulphates are sprayed on to foliage they are gradually decomposed by the carbon dioxide of the air with the formation of copper carbonate and some copper sulphate, according to the following equation:



<sup>1</sup> *Journ. Chem. Soc.* 1907, xci. 1988.

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To the soluble copper sulphate liberated in this way he attributes the main fungicidal action of Bordeaux mixtures.

A full account of the experiments on which this theory is based are to be found in the *Eleventh Report of the Woburn Experimental Fruit Farm*, 1910, pp. 22—36<sup>1</sup>. A stream of carbon dioxide was passed through Bordeaux mixtures of various compositions and the amount of copper appearing in solution was estimated at intervals varying from 30 minutes after the beginning of the experiment up to 8 days. With the compounds  $4\text{CuO}$ ,  $\text{SO}_3$  or  $10\text{CuO}$ ,  $\text{SO}_3$ , considerably more copper was dissolved than had been expected from the equation. The excess over the calculated amount is explained by the dissolution of the copper carbonate in the solution of copper sulphate and calcium sulphate formed during the reaction. With ordinary Bordeaux mixture, the amount of copper brought into solution was very small, the excess of lime being attacked by the  $\text{CO}_2$  much more readily than the basic sulphate of copper. Pickering therefore considers that Bordeaux mixtures made without excess of lime will be considerably more efficient than the ordinary mixture and will have an additional advantage in that there will be no delay in the initiation of the action.

While carrying out some experiments suggested by this work, it was found, most unexpectedly, that the whole of the copper brought into solution by the action of  $\text{CO}_2$ , for a short length of time, on the sulphate  $10\text{CuO}$ ,  $\text{SO}_3$ , was entirely reprecipitated in an insoluble form on removal of the  $\text{CO}_2$ ; and the bearing of this reaction on the question of the fungicidal action of Bordeaux mixtures has been investigated.

### *Action of $\text{CO}_2$ for a short period.*

The basic copper sulphates, in all the experiments to be mentioned, were prepared by the addition of the necessary amount of pure lime-water to copper sulphate solution and were always obtained precisely as described by Pickering. Carbon dioxide was then passed through the resulting mixture for 30 or 45 minutes, and after filtration the amount of soluble copper present at once determined<sup>2</sup>. On standing exposed to air, the dissolved copper in the filtrate began to reprecipitate almost at once and finally all was thrown out of solution in the form of a light blue scum and deposit.

<sup>1</sup> See also Pickering, *Journ. Agric. Sci.* Vol. III. p. 171.

<sup>2</sup> The potassium ferrocyanide colorimetric method, as detailed in Sutton's *Volumetric Analysis*, 8th ed. p. 213, was employed throughout and found to give very satisfactory results, the addition of ammonium nitrate to the liquids making the colour a more pronounced pink and rendering the test very sensitive.

The following table gives a few examples of the kind of results obtained:

TABLE I.

	Per cent. Cu in solution		
	Before treatment	After action of CO <sub>2</sub> for 30 minutes	After filtrate had stood over-night exposed to air
10CuO, SO <sub>3</sub> prepared from—			
1. Ordinary lime-water .....	0	·024	0
2. Pure lime-water .....	0	·022	0
3. Woburn paste .....	0	·015	0
4. 4CuO, SO <sub>3</sub> from pure lime-water	·0001	·022	* ·00014
5. 4CuO, SO <sub>3</sub> „ „ „	·00008	·028	* ·00005

\* Air passed through filtrate for 2 hours.

*The Basic Sulphate—10CuO, SO<sub>3</sub>.*

When the compound used was 10CuO, SO<sub>3</sub>, the reprecipitation of the dissolved copper was complete, occasionally in 12–18 hours but more often required 24–48 hours. If, however, a current of air was passed through the liquid, to hasten removal of the carbon dioxide, the whole of the copper came out of solution very rapidly in  $\frac{1}{2}$ –1 hour. The precipitated compound redissolved readily if carbon dioxide was again passed into the liquid, and while a saturated solution of CO<sub>2</sub> was maintained all the copper remained in solution; but as the gas was allowed to escape it began to be precipitated.

The reprecipitation is dependent on the removal of the carbon dioxide from the liquid as is shown by this experiment:

Carbon dioxide was passed into a Bordeaux mixture containing pure 10CuO, SO<sub>3</sub> for 25 minutes. There was then 0·02 per cent. Cu in solution. Various portions of this mixture were treated as follows:

	Per cent. Cu left in solution.
1. Air blown through for 20 mins. ... ..	·00065
2. „ „ 45 „ ... ..	0
3. After standing for 1 hour in open beaker <i>with frequent stirring and shaking</i> ... ..	·0042
4. Ditto for 24 hours ... ..	0
5. After standing for 1 hour in open beaker <i>without movement</i> ... ..	·0155
6. Ditto for 24 hours ... ..	·0072

Similar results were obtained with the filtrate from the mixture.

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It seems evident therefore that all the soluble copper in these experiments is in the form of a carbonate dissolved in the  $\text{CO}_2$  solution. Now, in order to explain this state of affairs it is necessary either to suppose that Pickering's equation for the action of  $\text{CO}_2$  on the basic sulphates is incorrect and that no copper sulphate as such is formed; or, that the copper sulphate set free according to the equation is removed from solution as it is formed. There is no doubt however that copper sulphate is formed (it can be detected in solution when  $4\text{CuO}, \text{SO}_3$  is the compound used); and the latter alternative is the explanation of what happens. Copper sulphate, up to a certain amount, cannot remain in solution in presence of any unchanged  $10\text{CuO}, \text{SO}_3$  but combines with it to form a lower insoluble basic sulphate (probably  $4\text{CuO}, \text{SO}_3$ ). This can be shewn to take place directly: *e.g.* in one experiment,  $10\text{CuO}, \text{SO}_3$  was prepared from 1 gm. pure  $\text{CuSO}_4$  and it was found that on gradually adding more  $\text{CuSO}_4$ , this was removed from solution up to 0.19 gm.

In another connexion, Pickering himself refers to this action, though the significance of his statement was not apparent until these experiments had been carried out. On p. 41 of the *Eleventh Report of the Woburn Experimental Fruit Farm*, 1910, he writes: "These basic sulphates may be converted one into another by the addition of either more lime or more copper sulphate...." It therefore appears that, though copper sulphate is formed, it is basic copper carbonate dissolved in the solution of  $\text{CO}_2$  which constitutes the copper in solution observed in these experiments.

### *The Basic Sulphate— $4\text{CuO}, \text{SO}_3$ .*

The case cannot be quite the same when  $4\text{CuO}, \text{SO}_3$  is treated with carbon dioxide. As it is the lowest basic sulphate prepared by Pickering, any normal copper sulphate set free cannot react with it and so be removed from solution. None the less, all the copper in solution after the action of  $\text{CO}_2$  for 30 minutes is reprecipitated on blowing air through the filtrate, though not so rapidly as in the case of  $10\text{CuO}, \text{SO}_3$ . (See Nos. 4 and 5 in Table I.) Soluble copper sulphate is undoubtedly formed since if the compound  $4\text{CuO}, \text{SO}_3$  precipitated by lime water and then washed entirely free from calcium sulphate, is submitted to the action of  $\text{CO}_2$  the filtrate afterwards shews the presence of sulphate, but as soon as all the dissolved copper has been reprecipitated, there is no longer any sulphate found in solution. Evidently therefore the copper sulphate produced in the reaction is

also in this case removed from solution by some means. It appears probable that it combines with the basic carbonate present to form a compound which is precipitated on removal of the  $\text{CO}_2$ ; and a reaction between copper sulphate and the basic carbonates of copper, precipitated by  $\text{Na}_2\text{CO}_3$  or  $\text{NaHCO}_3$ , can be shown to take place directly, though not very rapidly.

In one experiment, a solution containing .015 per cent. copper as copper sulphate was reduced to one of .0001 per cent. by shaking with a small quantity of washed basic carbonate of copper suspended in  $\text{CO}_2$ -free water. That the soluble copper was not absorbed by the filter paper was shewn by a control experiment. Possibly this may be a case of adsorption.

From these results, it will be seen that whether we start with the compound  $4\text{CuO}, \text{SO}_3$  or with  $10\text{CuO}, \text{SO}_3$ , after the action of  $\text{CO}_2$ , the same result is arrived at—any dissolved copper is in a form precipitable on removal of the  $\text{CO}_2$ .

*Action of  $\text{CO}_2$  for a longer period.*

The state of affairs is somewhat different when these basic sulphates are submitted to the *prolonged* action of  $\text{CO}_2$ . Starting with  $10\text{CuO}, \text{SO}_3$  which is a full blue bulky precipitate, the action of  $\text{CO}_2$  for 3–4 hours or longer produces enough carbonate and lower basic sulphate to change the general appearance of the precipitate—it becomes much denser and lighter blue. Under these conditions the copper going into solution is not all easily reprecipitated, particularly if the liquid be removed from contact with the precipitate. A number of experiments have been carried out, but as the conditions (*i.e.* prolonged contact with an atmosphere of  $\text{CO}_2$ ) are such that they can hardly affect the question of what occurs in practice, no more than this reference to them is necessary here.

It will be recognised that the results above described, though quite consistent with Pickering's work, are difficult to reconcile with the view that atmospheric carbon dioxide is the important factor in bringing into play the fungicidal properties of Bordeaux mixtures. It was therefore of interest to attempt to test this theory under conditions which approximated more nearly to those actually found in practice.

In the first place, ordinary air was passed through Bordeaux mixtures consisting of  $10\text{CuO}, \text{SO}_3$  or  $4\text{CuO}, \text{SO}_3$  with no excess of lime, for as long as 10 days; at the end of this time no trace of soluble

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copper was found in the filtrate. This result has been confirmed a number of times for periods extending from 1 to 5 days. When this experiment is carried out with a very small quantity of  $10\text{CuO}$ ,  $\text{SO}_3$  suspended in a fairly large bulk of water, the action of the  $\text{CO}_2$  in the air on the precipitate is indeed quite noticeable—the substance gradually turns a light green colour and becomes much less flocculent, i.e. it is largely converted into carbonate, and it shews effervescence with hydrochloric acid. There is evidently sufficient carbon dioxide in the air to convert most of the basic sulphate into carbonate under these circumstances, but not enough to dissolve a detectable amount of the carbonate. In such an experiment the liquid probably contains at least as much carbon dioxide as the film of water present on a leaf under normal conditions.

Again, never more than a very slight trace of copper (equivalent to less than  $\cdot 00003$  gm. Cu) was found in solution when Woburn Bordeaux mixture ( $4\text{CuO}$ ,  $\text{SO}_3$  or  $10\text{CuO}$ ,  $\text{SO}_3$ ) was allowed to stand exposed to air in a shallow layer in a dish for as long as 30 days; and the result was the same whether the film was kept moist with rain water or with ordinary tap water. This is at variance with the result of an experiment of Millardet and Gayon<sup>1</sup> in which a Bordeaux mixture containing no excess of lime exposed to rain on a filter paper showed copper in the filtrate in 7 days, and Schander<sup>2</sup>, carrying out a similar experiment, found copper in solution after 21 days. A possible explanation of the discrepancy of these results that suggests itself is connected with the question of filtration. Although the basic sulphates are retained by filter papers comparatively easily, yet when any carbonate has been formed, as would be the case here, it is sometimes a matter of great difficulty to ensure the filtrate being quite free from minute solid particles. From the conditions of Millardet and Gayon's experiment, it seems that incomplete filtration may possibly have accounted for their result.

If a thin layer of precipitated  $10\text{CuO}$ ,  $\text{SO}_3$  in a Petri dish is exposed to a moist atmosphere of  $\text{CO}_2$ , carbonate is formed and copper is dissolved as would be expected. On then exposing a dish treated in this way to the air for 2 days, only the slightest trace of soluble copper is to be found: that is to say, reprecipitation of any dissolved copper takes place under these conditions in the same manner as in the experiments previously described. This result has been obtained a number of times and it seems safe to conclude that it is only in presence of a large excess of carbon dioxide, such as could hardly occur out-of-doors, that an

<sup>1</sup> *J. d'Agr. Pract.* May 19, 1887.

<sup>2</sup> *Landw. Jahrb.* xxxiii. 1904, p. 517.

appreciable amount of copper is brought into solution from a film of Bordeaux mixture—and that only under those conditions would any copper so dissolved remain in solution.

Most of the experimental work has been carried out with Bordeaux mixtures prepared from pure copper sulphate and pure lime-water, in such amounts that the precipitate should be a definite compound of known composition, either  $4\text{CuO}, \text{SO}_3$  or  $10\text{CuO}, \text{SO}_3$ , with no excess of lime present to complicate matters.  $10\text{CuO}, \text{SO}_3$  is the compound present in the commercial Woburn Bordeaux paste, and the paste itself has been used to duplicate the experiments in a number of cases with results which have always been substantially the same as those obtained with the pure preparation.

As Pickering has shewn, the action of carbon dioxide on *ordinary* Bordeaux mixture is practically the same as on the no-excess-lime mixtures except that no copper appears in solution until nearly all the excess of lime has been carbonated. The insoluble compound present in ordinary Bordeaux mixture is  $10\text{CuO}, \text{SO}_3, 3\text{CaO}$ . If this compound is prepared free from any further excess of lime and is then submitted to the action of  $\text{CO}_2$ , the copper which is rendered soluble is entirely reprecipitated on removal of the  $\text{CO}_2$ , exactly as with the other basic sulphates. It therefore appears that all the arguments based on experiments with the no-excess-lime Bordeaux mixtures are applicable with at least equal force to the case of ordinary Bordeaux mixture.

The conclusion to which these experiments point is that, although the action of carbon dioxide in excess on the compounds present in Bordeaux mixtures brings copper into solution, yet it appears impossible to assign the fungicidal action to copper sulphate liberated by *atmospheric* carbon dioxide. It is difficult to apply experimental results directly to practical conditions because we have no accurate knowledge of the state of affairs in a film of dew or rain on the surface of a leaf; possibly traces of carbonate of copper are present in solution under some conditions; but that there should ever be enough carbon dioxide to dissolve more than very minute amounts seems most unlikely. A purely chemical explanation of the fungicidal action seems insufficient; and in the following paper reasons are put forward for believing that it is probably unnecessary to look for agencies by which the insoluble copper in Bordeaux mixtures is rendered soluble, and that actual contact between the fungus and the particles of the insoluble copper compound is the most important means by which germination or further growth is prevented.