THE AGEING OF BORDEAUX MIXTURE

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In a previous communication[1] it has been reported that freshly prepared alkaline Bordeaux mixture (5:5:50) consists of a gelatinous greenish-blue precipitate, which, in about 2 to 4 hours, changes to a deep blue solid. In the course of the present studies, it was observed that freshly prepared Bordeaux mixture contained a high initial concentration of copper in the aqueous phase (7 to 4 mg. cu. per l.) which decreased on standing to 0·50 mg. in 2 days. A further decrease to 0·47 mg. occurred, only very slowly. The results of a typical experiment are given in Table I. The general experimental procedure in this study was the same as has been described in the earlier paper.[1] Bordeaux mixture (5:5:50) was prepared by adding a 10% solution of copper sulphate to a well-stirred suspension of calcium hydroxide in a suitable amount of water. The precipitate was filtered at intervals, through a Jena sintered-glass filter I.G. 4, using the automatic filtering device. The aqueous phase was analysed for copper by the colorimetric method using sodium diethyl-dithio-carbamate and OH^-, CA^{++}; and SO_4^{--} were estimated by the usual analytical methods.

Table I

Ageing of Bordeaux Mixture at 24° C.

Period of ageing	Colour of precipitate	Copper in aqueous phase mg. Cu/l.	Total calcium in aqueous phase-mole per/l.	$Ca(OH)_2$ mole/l.	$CaSO_4$ mole/l.
1	2	3	4	5	6
1 hour ..	Greenish blue	4·21	0·0486	0·0195	0·0290
2 hours ..	do	2·69	0·0453	0·0196	0·0257
5 hours ..	Deep blue	0·59	0·0348	0·0195	0·0153
8 hours ..	do	0·56	0·0337	0·0195	0·0143
24 hours ..	do	0·53	0·0329	0·0197	0·0134
2 days ..	do	0·49	0·0326	0·0197	0·0128
5 days ..	do	0·48	0·0322	0·0197	0·0123
15 days ..	do	0·47	0·0321	0·0199	0·0123
1 month ..	do	0·47	0·0320	0·0199	0·0121
3 months ..	do	0·47	0·0324	0·0203	0·0122

From column 3, Table I, it will be noticed that there is a gradual decrease in the concentration of copper with time. The colour of the precipitate also

undergoes a change. The gelatinous greenish blue precipitate originally formed, changes to a compact deep blue solid after about 2 hours. This change in colour is accompanied by a fall in the concentration of copper in the aqueous phase.[1]

The ageing of precipitates is a well-known phenomenon and several crystalline precipitates have been found to undergo on ageing, a decrease in solubility. It was therefore considered to be likely that the fall in concentration of copper in the aqueous phase of Bordeaux mixture was due to ageing.

It will be seen from column 6, Table I, that the aqueous phase was initially supersaturated in regard to calcium sulphate. To eliminate any possible effect of this supersaturation on changes in copper concentration, the Bordeaux mixture was prepared under conditions wherein supersaturation with respect to calcium sulphate was obviated by taking appropriate quantities of water, copper sulphate and lime. To ensure however, that the aqueous phase was saturated in respect of calcium sulphate, a moderate excess of solid calcium sulphate dihydrate was added to the Bordeaux mixture, a few minutes after its formation, while the mixture was being vigorously stirred. Filtrates from this mixture were periodically collected and analysed. The results are given in Table II.

TABLE II

Ageing of unwashed Bordeaux mixture in water saturated with lime and calcium sulphate

Period of ageing	Colour of precipitate	Copper in aqueous phase mg. Cu/l.	Total calcium in aqueous phase-mole per/l.	$Ca(OH)_2$ mole/l.	$CaSO_4$ mole/l.
1	2	3	4	5	6
2 hours ..	Greenish blue	0·93	0·0322	0·0200	0·0123
5 hours ..	Deep blue	0·57	0·0321	0·0198	0·0124
24 hours ..	do	0·53	0·0322	0·0199	0·0125
5 days ..	do	0·48	0·0321	0·0199	0·0124
1 month ..	do	0·47	0·0322	0·0199	0·0124

A small quantity of the precipitate from the above mixture was filtered at a Jena sintered glass filter and rapidly washed with an aqueous solution saturated with calcium sulphate as well as with calcium hydroxide. The

precipitate was then allowed to age in a solution of the same composition as employed for washing the precipitate of Bordeaux mixture. Filtrates from the above mixture were collected at different intervals and analysed. The results are given in Table III.

TABLE III

Ageing of washed Bordeaux mixture in presence of water saturated with lime and calcium sulphate

Period of ageing	Colour of precipitate	Copper in aqueous phase mg. Cu/l.	Total calcium in aqueous phase-mole per/l.	$Ca(OH)_2$ mole/l.	$CaSO_4$ mole/l.
1	2	3	4	5	6
2 hours ..	Greenish blue	2·52	0·0335	0·0211	0·0124
5 hours ..	Deep blue	0·76	0·0328	0·0205	0·0123
24 hours ..	do	0·68	0·0326	0·0205	0·0123
5 days ..	do	0·63	0·0329	0·0204	0·0125
1 month ..	do	0·59	0·0328	0·0204	0·0124

A comparison of the data presented in Tables I, II and III shows that the initial supersaturation of the aqueous phase in regard to calcium sulphate, that normally occurs in the preparation of Bordeaux mixture, has little influence on the ageing of the Bordeaux mixture. The Bordeaux mixture that has been washed and then subjected to ageing in water saturated with calcium hydroxide and sulphate, seems to age a little more slowly as can be gathered from the copper values noted in column 3 of Tables II and III. From the above experiment, it may be concluded that the freshly formed precipitate has relatively a high solubility, due to the presence of fine primary particles. On standing, the fine particles undergo aggregation to larger units having a lower solubility.

A progressive decrease in the solubility of freshly prepared cupric hydroxide has been observed, on ageing, in several systems, as already reported in the earlier paper.[1] In all these cases, the variation of copper in solution, with time, is due to the phenomenon of ageing.

The rate of ageing of the precipitate in Bordeaux mixture is considerably influenced by temperature. This aspect was investigated by preparing samples of Bordeaux mixture at 0° C. and at 70±2° C. and studying the changes in the concentration of copper in these systems. The experimental results of the system at 0° C. are given in Table IV.

TABLE IV

Ageing of Bordeaux Mixture at 0° C.

Period of ageing	Colour of precipitate	Copper in aqueous phase mg. Cu/l.	Total calcium in aqueous phase mole per/l.	$Ca(OH)_2$ mole/l.	$CaSO_4$ mole/l.
1	2	3	4	5	6
3 hours ..	Greenish blue	13·0	..	0·0232	0·0274
24 hours ..	do	10·8	0·0505	0·0242	0·0262
5 daya ..	do	7·7	0·0502	0·0246	0·0259
15 days ..	Deep blue	0·96	0·0477	0·0231	0·0245
2 months ..	do	0·72	0·0348	0·0242	0·0108

In this system, copper in solution is found to decrease very slowly (Column 3, Table IV) showing that ageing takes place more slowly at 0° C. The initial concentration of copper (13 mg. Cu/litre) is higher than in the mixture prepared at room temperature (24° C.) because in the case of the system at 0° C., measurement of solubility could be made before any appreciable aggregation of the precipitate had taken place. It is also very significant that the transformation of the gelatinous greenish blue precipitate to the deep solid occurred at 0° C., 10 days after the preparation of the sample, while the same transition occurred in 2 to 4 hours at 24° C.

To investigate the system at a higher temperature, Bordeaux mixture was prepared at 70° and was maintained at that temperature by immersing the bottle containing it, in a water thermostat. The bottle was provided with a water-cooled condenser and a soda lime tube and the mixture was filtered at suitable intervals and analysed. The results are given in Table V.

The greenish blue precipitate formed in this case turned deep blue within an hour of its formation. A small part of the precipitate turned black in three hours but the bulk of the precipitate remained deep blue. The continuance of the deep blue colour, in spite of the presence of the black particles of cupric oxide, is evidence of the stabilising influence of calcium sulphate on Bordeaux mixture. Copper hydroxide, it may be pointed out, is stabilised even at 100° C. by small amounts of manganese sulphate and other salts.[2,3]

A comparison of the data presented in Table V with those of Table I indicates that the initial concentration of copper at 70° C. is lower than that

TABLE V

Ageing of Bordeaux mixture at 70° C.

Period of ageing	Colour of precipitate	Copper in aqueous phase mg. Cu/l.	Total calcium in aqueous phase-mole per/l.	$Ca(OH)_2$ mole/l.	$CaSO_4$ mole/l.
1	2	3	4	5	6
1 hour ..	Deep blue	1·49	0·0257	0·0114	0·0143
5 hours ..	do	0·46	0·0251	0·0128	0·0123
24 hours ..	do	0·42	0·0253	0·0130	0·0123
5 days ..	do	0·36	0·0256	0·0132	0·0124

in Bordeaux mixture at 24° C. and falls off rapidly with time, due to the increased rate of ageing.

SUMMARY

Bordeaux mixture (5: 5: 50) prepared at room temperature (24° C.) contains a high initial concentration of copper in the aqueous phase (4 to 7 mg. copper/litre). On keeping the mixture at 24° C. the copper content of the solution decreases, and in a few days, attains a steady value of 0·47 mg. copper per litre.

The changes in copper concentration of the aqueous phase are due to the ageing of the precipitate. Experiments conducted at 0° and at 70° C. show that an increase in temperature markedly promotes ageing.

In the initial stages of formation of Bordeaux mixture, the aqueous phase is supersaturated with calcium sulphate, but the supersaturation does not influence in any way the ageing of the precipitated Bordeaux mixture. If, soon after its formation, the Bordeaux mixture is washed with water saturated with lime and with calcium sulphate, the rate of ageing of the solid is slightly reduced.

REFERENCES

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