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by F. J. SCHNEIDERHAN

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Preparation and Properties of Bordeaux Mixtures * †

by F. J. SCHNEIDERHAN

Introduction

Bordeaux mixture is one of the oldest of fungicides. Its discovery marked an epoch in the development of plant-disease control, for it was the first fungicide to come into wide and general use to control infection by plant pathogens. A number of changes, particularly in the concentration of Bordeaux mixture, have been made during the 50 years that have elapsed since its discovery. The methods of combining copper sulphate and calcium hydroxide also have undergone changes, but a review of the literature on this subject shows that different investigators adhere to methods of their own, with the result that no standard, uniform method has been adopted.

The present publication describes some of the physical and chemical properties of "Instant Bordeaux" prepared from pulverized copper sulphate and high calcic hydrate, together with the methods of its preparation. The discussion compares these properties with those of Bordeaux mixture prepared from quicklime and low calcic hydrate.

History

The literature on Bordeaux mixture is extensive, and the important historical features of its development have been described so many times that only a brief mention of the main facts of its history will be made here.

The fungicidal properties of copper compounds were discovered by Prevost *(22)* in 1807. He demonstrated that a dilute solution of copper sulphate prevented germination of spores of *Tilletia tritici*. According to this author "the actual sulphate necessary to give water the power of preventing the smut from germinating at a low temperature does not exceed 1/400,000 of its weight, and 1/1,200,000 retards its germination."

In the literature of the 75 years following this discovery only occasional reference is made to the use of copper sulphate for treating seed wheat. In 1861 Radclyffe used a solution consisting of two ounces of copper sulphate in a bucket of water for the control of rose mildew, applying the solution with a watering pot.

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†The writer wishes to express his appreciation of the advice and suggestions given during the course of this study by Dean F. D. Fromme, Dr. C. R. Orton, Dr. L. H. Leonian, and Dr. J. H. Martens of West Virginia University.

The next mention of the use of copper compounds for fungicidal purposes is probably the most important because it was made by Millardet *(16)*, the discoverer of Bordeaux mixture. The fungicidal properties of this fungicide, known originally as "bouillie bordelaise", were discovered by accident in October 1882. The translation setting forth the details of this discovery is available in published form *(26)*.

The original Bordeaux mixture used by Millardet was of the formula 18-33-34 and had to be spread with a brush. This formula contained approximately six times the copper sulphate and twelve times the amount of lime per gallon of water contained in Bordeaux mixture of 4-4-50 formula.

The original formula of Bordeaux mixture soon was changed as a result of the work of Millardet and Gayon *(17)*, Mach *(15)*, Patrigeon *(19)*, and Gaillot *(8)*. A series of tests with different formulae ranging from approximately 25-50-50 to 4-1-50 by Millardet and Gayon proved that the fungicide with the lower concentration of copper sulphate and lime was as effective as that with the higher in preventing germination of Plasmopara spores.

According to the authors the last-mentioned formula was likely to cause foliage injury because the lime was just sufficient to precipitate all the copper, and if impure lime was used, unprecipitated copper would occur in the wash and would cause the injury.

In 1887 Bordeaux mixture was introduced into the United States by the U. S. Department of Agriculture. The formulae first recommended were 8-10-20, 16-30-29, and later 6-2-22. Crandall *(5)* states, "of 17 stations reporting in 1891, nine used the 6-4-22 formula; two used 6-4-25 formula: two, Ohio and New Jersey, used 4-4-50, the first mention I find of this formula. The other four each used a different formula, but all were weaker than the first given above." According to the same author the 22-gallon formula disappeared by 1896, and this date may be considered to mark the general adoption of the 50-gallon formula now in general use in America. During the past five years there has been a tendency in the East-Central States to adopt the 100-gallon formula, so that 4-4-50, commonly known as standard Bordeaux mixture, is expressed as 8-8-100.

The tendency from 1882 up to the present time has been to reduce the concentration of Bordeaux mixture. There is still a wide range of formulae for fruit and vegetable spraying, as a study of the spray recommendations in different states will reveal. For apple spraying, formula 4-12-50 is now used in Nova Scotia, while in the United States such formulae as 1-2-50, 2-4-50, 3-6-50, and 4-4-50 are used. For vegetables the 4-4-50 formula seems to be in general use. Recently Rosen *(23)* reported good control of blossom blight of apples with 1-3-50 Bordeaux mixture applied just before and during the blooming period.

Up to 1906, when the efficacy of lime-sulphur was demonstrated, Bordeaux mixture was practically the only fungicide used widely for orchard spraying. Today it is the general practice in the United States to use sulphur fungicides during the early growing season and Bordeaux mixture or some other copper-containing fungicide during hot weather, because Bordeaux mixture causes fruit russeting early in the season, while lime-sulphur and other sulphur sprays frequently cause fruit and leaf injury during hot weather.

Chemical and Physical Considerations of Bordeaux Mixture

There has been notable disagreement among investigators as regards the chemistry of Bordeaux mixture. The original investigators, Millardet and Gayon *(18)*, stated that copper in the mixture as well as on the leaves is found in the form of a hydrate or an oxide insoluble in pure water. This hydrate is eventually dissolved by rain water containing a small amount of carbonic acid.

The reaction which occurs when copper sulphate and calcium hydrate are combined is represented by the following equation:

$$CuSO_4 + Ca(OH)_2 = Cu(OH)_2 + CaSO_4$$

According to Fairchild *(7)* the first products of the above reaction are basic sulphates of copper, but when sufficient lime has been added to react with the copper sulphate, the resulting compound is hydroxide of copper, $Cu(OH)_2$.

The work of Pickering *(20)*, *(21)* and of the Duke of Bedford *(1)* shows that lime water added to copper sulphate gives a precipitate of a blue basic sulphate which increases in basicity with the addition of lime. When an excess of lime is added, the result is a series of double sulphates and eventually a double oxide. When strong alkalis are used, hydroxides are formed, but if calcium hydroxide is used, basic sulphates are always formed, except in the presence of an excess of calcium hydroxide. Pickering states that the following basic salts may result from the interaction of copper sulphate and calcium hydroxide. The equations for the formation of these distinct basic salts are as follows:

$$4\ CuSO_4 + 3\ Ca(OH)_2 = 4\ CuO.SO_3 + 3\ CaSO_4$$
$$5\ CuSO_4 + 4\ Ca(OH)_2 = 5\ CuO.SO_3 + 4\ CaSO_4$$
$$10\ Cu\ SO_4 + 9\ Ca(OH)_2 = 10\ CuO.SO_3 + 9\ CaSO_4$$
$$10\ CuSO_4 + 12\ Ca(OH)_2 = 10\ CuO.SO_3\ 3CaO + 9\ CaSO_4$$

The basic sulphates 4 $CuO.SO_3$ and 5 $CuO.SO_3$ are partly soluble in the mother liquor, the former to the extent of 1 part in 40,000 and the latter, 1 to 2 parts per million.

According o Butler *(2)* "the basic sulphates also show well-marked differences when subjected to the action of heat. In the case of 4 $CuO.SO_3$ and 5 $CuO.SO_3$, the change brought about by boiling is similar to that which occurs in these salts on standing; they become denser and in the case of 4 $CuO.SO_3$, greener. The basic salt 10 $CuO.SO_3$, on the other hand, turns completely black, owing to the formation of cupric oxide, but 10 $CuO.SO_3$, 3 CaO is not affected."

It is not known whether Bordeaux mixtures are "mixtures" or definite chemical compounds. According to Holland, Dunbar, and Gilligan *(10)*, "Whether the copper precipitates are chemical entities or mixtures is diffiicult to determine, owing to their instability and the presence of insoluble by-products, but, in the last two instances (double sulphate and double oxide), the compounds designated are empirical."

In the chemical studies of Bordeaux mixtures made by Pickering *(21)*, lime-water was used because it was nearly impossible to make an accurate chemical analysis on account of impurities in milk of lime. The chemistry of Bordeaux mixture prepared from lime-water is fairly well known, but the assumption is questionable that the facts obtained on that basis are analogous to those that result from the use of milk of lime, which usually contains magnesium compounds and silicates. Nevertheless, the present accepted chemistry of Bordeaux mixture is based largely on the study of the fungicide prepared from lime-water and copper-sulphate solution.

Certain Problems of Mixing Bordeaux Mixture

Any reviewer of the literature of Bordeaux mixture will be impressed by at least two conditions that need modification. In the first place there are too many different formulae and in the second place there is a multiplicity of mixing methods out of all proportion to the simple needs of the case. There is probably no need for a higher concentration than 4-4-50 Bordeaux mixture for vegetable diseases and 2-2-50 or even less for apple diseases. Holland *(10)* and others have described, and tested the results of, at least 12 methods of combining copper sulphate and lime solutions to make Bordeaux mixture. From this and other studies it is obvious that possibly three methods deserve consideration: viz., dilute copper-sulphate solution added to concentrated lime solution; equal parts of the diluted components poured simultaneously into the spray tank; and lastly, concentrated lime solution added to dilute copper-sulphate solution. There is no significant difference in the quality of Bordeaux mixture resulting from these three methods, any one of which could be adopted the world over and result in a simplification and standardization of the mixing process.

In the discussions to date of Bordeaux mixture the mixing operation usually concerns the handling of stock solutions of copper sulphate and quicklime. Due to the variations in the composition of limestone from which quicklime and hydrated lime are made, the latter also varies in composition, particularly in the CaO and MgO content. Investigators generally agree that lime high in CaO is desirable for making Bordeaux mixture. When hydrated lime contains 70% or more of CaO and quicklime 95% or more, such limes are considered to be high in CaO. Pebble lime and powdered quicklime made in rotary lime kilns are the best quicklimes to use in preparing this fungicide because they slake rapidly and leave very little grit and unslaked lime if the proper procedure is followed.

If stock solutions of copper sulphate and quicklime having a high CaO content are combined in a proper manner, good Bordeaux mixture will result. However, certain inherent difficulties connected with making Bordeaux mixture from stock solutions have resulted not only in an unsatisfactory fungicide but also in a growing reluctance among fruit growers and truck gardeners to use it.

The chief difficulty of this method of making Bordeaux lies in slaking the quicklime. When too much water is used the lime "drowns;" when too little is used it "burns." In both cases a considerable part of the original weight of lime remains in the form of unslaked lumps and gritty material unsuitable for making this fungicide. Orchardists often fail to strain the milk of lime, and frequently, when it is strained, the wire screen on the spray tank is used. The average size of the mesh in these screens is 16 to 20 per inch, which is too large for straining a gritty milk of lime.

Failure to slake quicklime properly and to strain the milk of lime through suitable cloth or wire screens results in a Bordeaux mixture containing particles of pure lime coated with a layer of Bordeaux mixture, together with coarse grit, all of which clogs spray nozzles and tank outlet screens and adds to the cost of spraying. Furthermore, spraying gritty Bordeaux mixture at pressures ranging from 500 to 600 pounds per square inch may result in mechanical injury to fruit and foliage, especially when the spray gun or rod is directed continuously at one section of a tree.

Agricultural hydrate has been used for making Bordeaux. Most of the so-called agricultural hydrates are too coarse for this purpose, and the results when such lime has been used have usually been unsatisfactory.

During the past six years the writer has studied the use of pulverized copper sulphate and high calcic hydrate commonly known as chemical hydrated lime for preparing Bordeaux mixture. Before discussing the details of these studies brief mention will be made of the use of hydrated lime for making Bordeaux mixture.

According to Butler *(2)*, hydrated lime and copper sulphate produce a Bordeaux mixture that differs somewhat from that obtained from quicklime if the limestones from which both types of lime were derived are of the same degree of purity. This author reports lower suspension in Bordeaux prepared from hydrated lime and ascribes this to the coarser nature of the milk of lime prepared from hydrated lime. Neither chemical analysis nor a description of the physical characteristics of the hydrated lime is given.

Holland and associates *(10)* used four different forms of lime, in different ratios, with copper sulphate and studied the suspension of the resulting Bordeaux mixtures. Their conclusion is as follows: "Four forms of lime (lime-water, chemically precipitated lime, milk of lime, and commercial hydrated lime) were employed in preparing Bordeaux and allied mixtures. The activity varies directly as the degree of dispersion and decreases in the order named. Some of the better grades of hydrated limes are promising substitutes for milk-of-lime but require soaking before being used."

An examination of the data prepared by these authors shows that the suspension percentages at the 1, 2, and 3-hour periods for 4-2-50

Bordeaux mixture prepared from milk-of-lime were 97.5, 95.0, and 92.6 respectively, while the Bordeaux prepared from hydrated lime showed percentages of 96.4, 92.7, and 89.0. This is not a wide difference. The authors do not state whether the hydrated lime was ordinary hydrate or chemical hydrated lime.

No doubt ordinary hydrated lime has been used for preparing Bordeaux mixture for some time. In 1916 Sanders *(21)* described a method in which hydrated lime and pulverized copper sulphate were used for making Bordeaux mixture in Nova Scotia. This is the first mention of the use of powered ingredients for making Bordeaux mixture. A letter from this author states that this Bordeaux mixture was known locally as "quick-time Bordeaux". The essential features of preparing this type are similar to the method of making "Instant Bordeaux" *(25)*. There are two important differences: the use of regular hydrated lime in Nova Scotia in contrast to the use of superfine chemical hydrated lime by the writer, and the dumping of the pulverized copper sulphate into the empty spray tank, a practice which was found to be unsatisfactory.

Powdered Bordeaux mixtures have been sold in the United States under proprietary names. Usually such a material is a mixture of hydrated lime and anhydrous pulverized copper sulphate. Unsatisfactory results have sometimes followed the use of these powdered Bordeaux mixtures because they usually deteriorate in storage and their cost has been excessive for orchard use.

Suspension Tests

The literature of Bordeaux mixture shows frequent use of suspension or sedimentation tests as criteria for judging the fungicidal efficiency and quality of this fungicide. This has been true particularly of American investigators in their study of the effect of different mixing methods on the resulting Bordeaux mixture. The suspension test seems to have been the means of determining the effects of temperature, concentration, different amounts and forms of lime, and supplementary materials on Bordeaux mixture.

Only one phase of the study of Bordeaux mixture — the method of mixing — will suffice to show that investigators frequently have resorted to the suspension test as the measure of quality of this fungicide. Holland, Dunbar, and Gilligan *(10)* have prepared a table showing the effects on suspension obtained by other authors who used various methods of mixing copper sulphate and lime. This table, to which have been added the data obtained by Holland, is presented to show that the suspension test of Bordeaux mixture has been considered reliable by a number of recognized investigators.

In Table 1 will be found a summary of suspension tests made by Butler *(4)*, Hawkins *(9)*, Jones *(12)*, Pickering *(1)*, Warren and Voorhees *(27)*, and Holland, Dunbar, and Gilligan *(10)*.

TABLE 1—*Ratio of volumes of suspended Bordeaux to total volume of liquid observed by investigators when different methods of mixing were used*

Method Number	Butler 4-4-50		Hawkins 4-3-50		Jones 7.5-5-50		Pickering 3.2-3.2-50		Warren and Voorhees 4-4-50		Holland *et al.* 4-2-50	
	1 hr.	2 hr.	1 hr.	2 hr.	1 hr.	2 hr.	1 hr.	2 hr.	1 hr.	2 hr.	1 hr.	2 hr.
1	88.5%	70.9%	70.3%	...	87.0%	...	98.0%	90.0%	68.2%	...	93.8%	88.3%
2	92.7	86.3	...	...	87.0	...	93.0	64.0	...	...	97.0	94.7
3	94.8*	89.5	...	...	...	...	...	...	...	...	97.3	95.1
4	92.6	85.3	80.5	...	85.0	...	54.0	43.0	79.5*	...	97.5	95.2
5	93.9	88.7	...	...	96.0*	...	69.0	54.0	...	...	97.7	95.7*
6	91.2	82.9	...	...	...	...	...	...	...	...	93.4	86.8
7	...	...	...	...	...	...	...	...	...	...	95.9	92.1
8	92.0	84.6	97.1*	...	87.0	...	...	...	68.2	...	97.2	94.8
9	...	...	...	...	...	...	...	...	...	...	97.3	95.4
10	72.7	47.2	...	...	...	...	30.0	25.0	...	...	95.7	90.2
11	76.6	54.9	...	...	48.0	...	27.0	22.0	22.7	...	95.7	85.8
12	...	...	...	...	...	...	...	...	...	...	95.2	79.1

*Highest suspension.

EXPLANATION OF MIXING METHODS

1. Concentrated solution of copper sulphate into dilute solution of lime.
2. A solution of copper sulphate poured into lime solution of equal concentration.
3. Dilute copper-sulphate solution poured into concentrated lime solution.
4. Concentrated lime solution poured into dilute copper-sulphate solution.
5. A solution of lime added to a copper-sulphate solution of equal concentration.
6. Dilute lime solution added to concentrated copper-sulphate solution.
7. Concentrated copper-sulphate solution and dilute lime solution poured simultaneously into a third receptacle.
8. Equal concentrations of copper sulphate and lime solutions poured simultaneously into a third receptacle.
9. Dilute copper-sulphate and concentrated lime solutions poured simultaneously into a third receptacle.
10. Concentrated copper-sulphate solution added to concentrated lime solution and then diluted.
11. Concentrated lime solution added to concentrated copper sulphate solution and then diluted.
12. Concentrated solutions of copper sulphate and lime poured simultaneously into a third receptacle and then diluted.

There is general agreement among investigators that the physical properties of Bordeaux mixture are of greatest importance in determining its fungicidal efficiency. According to Holland *(11)* "the efficiency of insoluble copper fungicides is dependent largely on the degree of dispersion and other physical characteristics, as determined by suspension, which is undoubtedly the simplest and most practical method of evaluation. Wetting, spreading, and adhesiveness are so closely correlated and interdependent that complete differentiation is impossible."

According to Butler and Smith *(4)* "the effect of the temperature of the water with which Bordeaux mixture is made has but little influence on adhesiveness. The opinion that adhesiveness of a Bordeaux mixture can be judged from a sedimentation test is not, therefore, as reliable an index as has been thought."

Suspension tests undoubtedly constitute a simple and practical method of judging the physical properties of Bordeaux mixture, but should not be considered absolute criteria of fungicidal efficiency. The latter should be determined by spraying experiments supplemented by laboratory tests of toxicity with spores of pathogenic fungi.

Scope of This Study

Materials and Procedure

In the present study three types of lime and two forms of copper sulphate were used in the preparation of Bordeaux mixture of different formulae which were tested for suspension quality. The three types of lime were a quicklime from a rotary kiln, known to the lime trade as pebble lime; high calcic hydrate, known as chemical hydrated lime; and low calcic hydrate, commonly known as finishing lime. Two types of copper sulphate, the lump form commonly known as bluestone, and the pulverized form, which is very finely ground lump bluestone, were used. The suspension studies reported herein included 140 separate tests of Bordeaux mixture of 43 different formulae for periods ranging from one-half hour to three hours for each test. In addition, the effects of the age of the lime solution and of the use of supplements such as sugar, bentonite, and tannic acid on Bordeaux suspension were investigated. Certain facts in connection with the deterioration of Bordeaux mixture are presented. Toxicity studies under field and laboratory conditions were also part of this study, but discussions of these will be presented in another publication.

Recent studies on the effects of the form of lime on the resulting Bordeaux mixture *(10)* show that the chemical composition and physical characteristics of the lime are of prime importance. For this reason a description of the different limes used in these experiments follows:*

Quicklime (Pebble type)

Insoluble Sil. residue	1.30%
Fe_2O3 and Al_2O_3	.36
CaO	96.48
MgO	1.25
Loss on ignition	.52
Available (lime)	94.56
Unslakable residue	.62

*The writer acknowledges with thanks the cooperation of the American Stone and Lime Co., Bellefonte, Pa.; The Woodville Lime Products Co., Toledo, Ohio; and the Nichols Copper Co., New York, N. Y., in furnishing materials and chemical analyses used in this study.

Superfine Chemical Hydrate

Insol. Sil. Residue	.48%
Fe_2O_3 and Al_2O_3	.26
CaO	73.49
MgO	.86
Loss on ignition	24.76
Available CaO	71.06
$Ca(OH)_2$	93.92

Physical Properties

100% through 100-mesh sieve
99.95% through 200-mesh sieve
99.50% through 325-mesh sieve

Hydrated Finishing Lime

SiO_2	Trace
Fe_2O_3 and Al_2O_3	Trace
CaO	52.67
MgO	30.03
SrO	Trace
CO_2	1.30
P_2O_5	Trace
Chemically combined water	15.88
Hygroscopic water	Trace

Physical Properties

99% through 200-mesh screen
Volume: 58 cu. in. per pound

Commercial copper sulphate is sold in several forms, among which are the lump form known commonly as bluestone or blue vitriol, the pulverized form, and the form known commercially as "snow". Pulverized copper sulphate, as previously stated, is simply the finely-ground form of the chemical. Its fineness is such that all will pass through an 80-mesh screen and most of it will pass through a 100-mesh screen. The large copper manufacturers began to pulverize the product about 15 years ago. The demand for this material has greatly increased in recent years as a result of its use in the preparation of Instant Bordeaux.

Snow is not ground or pulverized but is a product of special crystallization. In size its particles approximate finely granulated sugar but will pass a 16-mesh screen. The original use of snow was in the manufacture of glue, cement, waterproofing materials, and concrete, but today the chief demand is from agriculture, particularly for making fungicides, and this demand is increasing. Snow has been used extensively in preparing Instant Bordeaux, but pulverized copper sulphate is better suited for this purpose because its greater fineness causes it to dissolve more quickly.

The analysis of the pulverized copper sulphate used in these experiments is as follows:

Copper	25.33%	present as $Cu\ SO_4 . 5H_2O$ (99.50%)
Nickel	.08	present as $Ni\ SO_4 . 6H_2O$ (.36%)
Iron	.026	present as $Fe\ SO_4 . 7H_2O$ (.13%)
Chlorine	.005	
Arsenic	.0035	
Antimony	.004	

Different methods of slaking the quicklime were tried, but the best results were obtained by adding 1 part of pebble lime to 2 parts of hot water and diluting with hot water. This lime slakes immediately with explosive violence, and it was found necessary to begin dilution immediately, with constant stirring to eliminate excessive heat in "pockets". The object of slaking was to effect complete hydration, which is accompanied by a high degree of dispersion. The resulting milk of lime contained very little grit and unslaked material, as was shown by the residue on the cheese cloth through which every batch was strained. The milk of lime was standardized so that 1 gm. of lime was suspended in 10 c.c. of water.

For the suspension tests all formulae of Bordeaux mixture were prepared in 1000-c.c. batches. In the beginning the proper amount of chemical hydrate was added to 250 c.c. of water, and the proper amount of pulverized copper sulphate was added to 750 c.c. of H_2O after sufficient stirring to disperse the lime and dissolve the copper sulphate; then the lime solution was poured slowly with constant stirring into the copper-sulphate solution.

A 500 c.c. sample was then poured into a 500 c.c. graduate of the following average dimensions: total height, 360 mm; height of 500 graduation, 280mm; inside diameter, 48 mm; graduations at 5 c.c. intervals.

Numerous suspension tests indicated no significant difference in suspension percentages of Bordeaux mixture prepared by the method just described from those resulting from standardized suspensions and solutions of hydrated lime and copper sulphate respectively. With this fact in mind, the weighing of small quantities of dry hydrated lime and copper sulphate was discontinued. The solutions were standardized to contain 1 gm. of hydrated lime or copper sulphate in 10 c.c. of water, which resulted in a considerable saving of time.

Suspension tests of from 10 to 13 formulae of Bordeaux mixture were run simultaneously. In no case were two 500-c.c. samples from the same 1000-c.c. batch used to obtain the average suspension percentage. When triplicate suspension tests showed uniformity in results, the averages were considered to be representative. In the series based on 1 pound of copper sulphate and varying amounts of lime, the reactions were somewhat irregular; in such instances the average of six tests was used as the suspension percentage.

It was found necessary to standardize the manual operations throughout to get uniform results; consequently the same half-gallon Mason jars were used to contain 750 c.c. of copper-sulphate solution, into which was poured slowly 250 c.c. of diluted milk of lime. The mixture was then stirred with the same paddle, using 25 similar strokes for a duration of 25 seconds. The resulting Bordeaux mixtures of different formulae were poured into glass pitchers to facilitate pouring into the graduates. The pitchers were held at the same height above a funnel with a 10 mm opening, to assure uniformity in drop while filling the graduates. As regards the stirring of Bordeaux mixture it might be said that the work of Jones *(12)* indicates that long stirring aids suspension.

A thorough stirring and not a prolonged stirring was considered to be sufficient by the Duke of Bedford and by Pickering *(1)*. The results of Butler's *(2)* study of prolonged stirring were borne out by the work of the writer; namely, that prolonged stirring of Bordeaux mixture is unnecessary and that one thorough stirring of 25 seconds is sufficient to give complete dispersion and a maximum of suspension. All tests were made with the original temperature of the Bordeaux varying from 21-23° C. These temperatures did not vary more than a few degrees during the three hours because the tests were made in a basement laboratory, where air temperatures were fairly constant, varying only from 20° to 23° on some days and showing less variation on other days. It is known that increase in the temperature accelerates settling and deterioration of Bordeaux mixture.

In the following tables and discussion Bordeaux formulae will be expressed on the basis of pounds of copper sulphate and lime used in 50 gallons of water. Thus 4-4-50 means 4 pounds of copper sulphate and 4 pounds of lime in 50 gallons of water.

As the following tables indicate, in all instances the lowest ratio of copper sulphate to lime was 1:0.5. In field practice the weight of lime in Bordeaux mixture is usually greater than that of copper sulphate because an excess of lime is generally believed to reduce the caustic properties of the fungicide.

The tests were arranged in series varying from 1 to 4 pounds of copper sulphate in 50 gallons of water. With the copper sulphate content constant for one series, the various formulae were obtained by varying the weight of lime. Suspension is expressed in percentage, based on the height of the column of suspended material to total height.

Experimental Results

Suspension Tests with Bordeaux Mixture

The following tables contain the data on suspension tests of Bordeaux mixture prepared from different quantities and forms of copper sulphate and different quantities and forms of lime. For convenience, reference is made to a series containing 1 pound of copper sulphate to 50 gallons of water as the 1-pound series, 2 pounds as the 2-pound series, etc. The suspension tests of the same series of Bordeaux formulae prepared from three different forms of lime will be considered together. Thus Table 2 contains the suspension data of the 1-pound series for low calcic hydrate, high calcic hydrate, and quicklime, respectively.

The suspension percentages at the half-hour period were compared in the 1-pound series because rapid deterioration occurs later, especially after two hours. When low calcic hydrate was used, the highest suspension occurred in formula 1-1.5-50 and the lowest in formula 1-0.5-50. When high calcic hydrate was used, the highest suspension occurred in formula 1-1-50 and the lowest in 1-5-50. In the case of quicklime, formula 1-1.5-50 gave the highest suspension and 1-5-50 the lowest. In formula 1-0.5-50, prepared from low calcic hydrate, the results were somewhat erratic, the Bordeaux being of a thin, flocculent texture and non-gelatinous. In Nos. 2 and 3 for all three forms of lime the consistency of the Bordeaux was gelatinous, but deterioration, as evidenced by color changes and rapid settling, became pronounced. One of the highest suspensions in Table 2 occurred in No. 2, formula 1-1-50, in which the forms of lime and copper sulphate are those used to prepare Instant Bordeaux. An excess of lime beginning at No. 4, formula 1-2-50, caused a bulky precipitate which seemed to settle out at a rate somewhat proportionate to this excess.

TABLE 2—*Comparison of suspension percentages of Bordeaux mixture prepared from one* (1) *pound of copper sulphate and different quantities and forms of lime at* ½, 1, 1½, *and 2-hour intervals*

No.	Formula	Copper Sulphate	Lime	½ hr.	1 hr.	1½ hrs.	2 hrs.
		(1) Pulv.	Low Calc. Hydrate	27.0%	20.0%	16.0%	15.0%
1.	1-0.5-50	(2) Pulv.	High Calc. Hydrate	73.0	31.0	24.0	20.0
		(3) Lump	Quicklime	73.0	49.0	41.0	32.0
		(1) Pulv.	Low Calc. Hydrate	75.0	54.0	41.0	35.0
2.	1-1-50	(2) Pulv.	High Calc. Hydrate	94.0	85.0	78.0	67.0
		(3) Lump	Quicklime	93.0	67.0	55.0	44.0
		(1) Pulv.	Low Calc. Hydrate	85.0	70.0	56.0	49.0
3.	1-1.5-50	(2) Pulv.	High Calc. Hydrate	94.0	85.0	77.0	66.0
		(3) Lump	Quicklime	94.0	72.0	60.0	51.0
		(1) Pulv.	Low Calc. Hydrate	73.0	54.0	46.0	41.0
4.	1-2-50	(2) Pulv.	High Calc. Hydrate	86.0	69.0	60.0	53.0
		(3) Lump	Quicklime	91.0	66.0	52.0	47.0
		(1) Pulv.	Low Calc. Hydrate	61.0	43.0	38.0	34.0
5.	1-2.5-50	(2) Pulv.	High Calc. Hydrate	71.0	56.0	49.0	44.0
		(3) Lump	Quicklime	78.0	60.0	52.0	47.0
		(1) Pulv.	Low Calc. Hydrate	51.0	39.0	34.0	31.0
6.	1-3-50	(2) Pulv.	High Calc. Hydrate	62.0	51.0	45.0	39.0
		(3) Lump	Quicklime	79.0	61.0	52.0	47.0
		(1) Pulv.	Low Calc. Hydrate	45.0	35.0	31.0	28.0
7.	1-3.5-50	(2) Pulv.	High Calc. Hydrate	57.0	38.0	32.0	28.0
		(3) Lump	Quicklime	53.0	41.0	37.0	32.0
		(1) Pulv.	Low Calc. Hydrate	43.0	34.0	30.0	27.0
8.	1-4-50	(2) Pulv.	High Calc. Hydrate	51.0	34.0	29.0	25.0
		(3) Lump	Quicklime	47.0	37.0	33.0	31.0
		(1) Pulv.	Low Calc. Hydrate	34.0	30.0	26.0	24.0
9.	1-4.5-50	(2) Pulv.	High Calc. Hydrate	45.0	30.0	26.0	23.0
		(3) Lump	Quicklime	42.0	34.0	31.0	28.0
		(1) Pulv.	Low Calc. Hydrate	34.0	27.0	24.0	22.0
10.	1-5-50	(2) Pulv.	High Calc. Hydrate	42.0	29.0	25.0	22.0
		(3) Lump	Quicklime	41.0	34.0	30.0	27.0

There is no significant difference between the suspension of Bordeaux prepared from quicklime and that from high calcic hydrate. This seems to indicate comparable activity of these forms of lime The data show that in all instances low calcic hydrate gave lower suspension than the other two forms of lime in the 1-pound series. The rapid settling out in No. 1 is probably due to deterioration accompanied by a change in color from green to purple and the formation of spherulites which will be discussed later. The concentration of copper and lime in the 1-pound series is not sufficient to produce the smooth, gelatinous precipitates and high suspensions found in higher concentrations.

Figures 1, 2, and 3 show typical suspension tests of ten formulae of the 1-pound series prepared from stock solutions of lump copper sulphate and quicklime. Since the data in the tables are based on the average of at least three tests and in some instances six, no exact agree-

FIGURES 1, 2, and 3

Suspension tests of ten formulae of Bordeaux mixture prepared from stock solutions of copper sulphate and quicklime.

No. 1 1-0 5-50
No. 2 1-1-50
No. 3 1-1.5-50
No. 4 1-2-50
No. 5 1-2.5-50
No. 6 1-3-50
No. 7 1-3- 5-50
No. 8 1-4-50
No. 9 1-4.5-50
No. 10 1-5-50

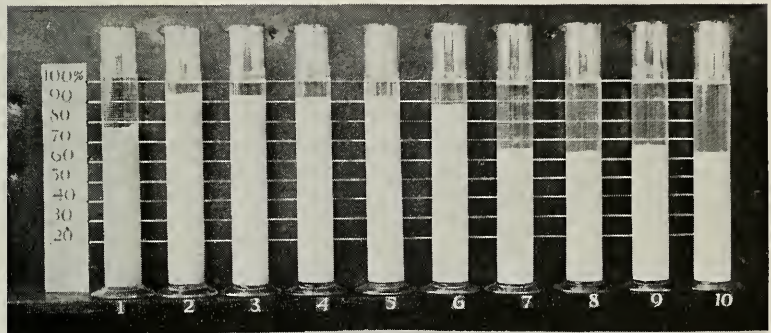

FIG. 1 -- After 1 hour

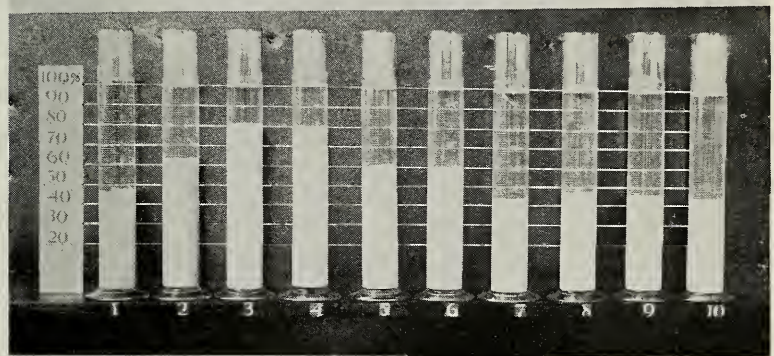

FIG. 2 -- After 2 hours

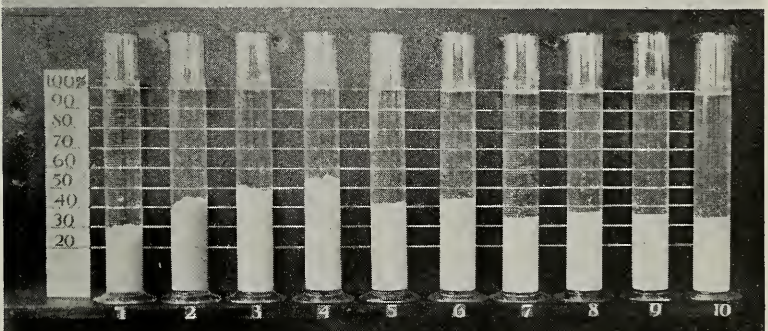

FIG. 3 -- After 3 hours

ment can be expected between the tabulated data and any particular test shown in the photographs.

It is evident in the 2-pound series that the average suspension percentage for all formulae was considerably higher than in the 1-pound series. When low calcic hydrate was used, the highest average suspension occurred in formula 2-2.5-50 and the lowest in 2-1-50. When high calcic hydrate was used, the highest average suspension for the 3-hour period occurred in formula 2-1.50-50 and the lowest in 2-5.5-50. In the case of quicklime the highest average suspension was found in formula 2-1-50 and the lowest in 2-5.5-50. The highest average suspension of the 30 tests in Table 3 occurred in formula 2-1.5-50, when high calcic hydrate was used. It is evident that the high suspension range in Bordeaux prepared from high calcic hydrate is wider than that shown by the two other forms of lime.

TABLE 3—*Comparison of suspension percentages of Bordeaux mixture prepared from two (2) pounds of copper sulphate and different quantities and forms of lime at ½, 1, 1½, 2, and 3-hour intervals*

No.	Formula	Copper Sulphate	Lime	½ hr.	1 hr.	1½ hrs.	2 hrs.	3 hrs.
		(1) Pulv.	Low Calc. Hydrate	66.0%	50.0%	42.0%	37.0%	33.0%
		(2) Pulv.	High Calc. Hydrate	98.0	97.0	95.0	93.0	90.0
1.	2-1-50	(3) Lump	Quicklime	98.0	94.0	83.0	70.0	49.0
		(1) Pulv.	Low Calc. Hydrate	90.0	65.0	51.0	46.0	41.0
		(2) Pulv.	High Calc. Hydrate	98.0	97.0	96.0	95.0	92.0
2.	2-1.5-50	(3) Lump	Quicklime	98.0	94.0	78.0	60.0	42.0
		(1) Pulv.	Low Calc. Hydrate	97.0	94.0	88.0	80.0	71.0
3.	2-2-50	(2) Pulv.	High Calc. Hydrate	98.0	97.0	96.0	94.0	90.0
		(3) Lump	Quicklime	98.0	93.0	68.0	50.0	31.0
		(1) Pulv.	Low Calc. Hydrate	98.0	95.0	93.0	89.0	72.0
4.	2-2.5-50	(2) Pulv.	High Calc. Hydrate	98.0	97.0	95.0	93.0	88.0
		(3) Lump	Quicklime	97.0	90.0	64.0	49.0	31.0
		(1) Pulv.	Low Calc. Hydrate	98.0	95.0	89.0	81.0	55.0
5.	2-3-50	(2) Pulv.	High Calc. Hydrate	98.0	97.0	94.0	92.0	86.0
		(3) Lump	Quicklime	98.0	86.0	61.0	46.0	27.0
		(1) Pulv.	Low Calc. Hydrate	98.0	93.0	83.0	67.0	46.0
6.	2-3.5-50	(2) Pulv.	High Calc. Hydrate	98.0	96.0	94.0	91.0	85.0
		(3) Lump	Quicklime	97.0	82.0	57.0	44.0	24.0
		(1) Pulv.	Low Calc. Hydrate	97.0	93.0	84.0	72.0	44.0
7.	2-4-50	(2) Pulv.	High Calc. Hydrate	98.0	95.0	92.0	89.0	80.0
		(3) Lump	Quicklime	95.0	78.0	55.0	42.0	24.0
		(1) Pulv.	Low Calc. Hydrate	97.0	92.0	74.0	57.0	44.0
8.	2-4.5-50	(2) Pulv.	High Calc. Hydrate	97.0	95.0	92.0	89.0	77.0
		(3) Lump	Quicklime	94.0	73.0	53.0	41.0	22.0
		(1) Pulv.	Low Calc. Hydrate	95.0	82.0	65.0	54.0	41.0
9.	2-5-50	(2) Pulv.	High Calc. Hydrate	98.0	95.0	92.0	88.0	79.0
		(3) Lump	Quicklime	90.0	61.0	46.0	38.0	20.0
		(1) Pulv.	Low Calc. Hydrate	95.0	83.0	58.0	49.0	39.0
10.	2-5.5-50	(2) Pulv.	High Calc. Hydrate	97.0	94.0	88.0	81.0	67.0
		(3) Lump	Quicklime	88.0	65.0	48.0	35.0	20.0

In none of the tests in Table 3 was there evidence of free lime in suspension in contrast to free lime in the 1-pound series. The use of high calcic hydrate was followed by more uniform results than from the other forms of lime. The rapid drop in suspension in Bordeaux mixture prepared from quicklime after the 2-hour period seems to indicate more rapid deterioration than occurred in Bordeaux prepared from the hydrated limes. This is at variance with Butler's *(3)* observation and it should be stated that the high calcic hydrate and quicklime used in all the tests herein reported were manufactured in the same lime plant and from the limestone. A comparison of suspensions of Bordeaux made from high calcic hydrate and quicklime after 2 hours is shown in Figures 4 and 5.

FIGURES 4 and 5

Comparison of suspension in ten formulae of Bordeaux made from high calcic hydrate and quicklime after 2 hours.

No. 1	2-1.-50	No. 5	2-3.-50	No. 9	2-5.-50
No. 2	2-1.5-50	No. 6	2-3.5-50	No. 10	2-5.5-50
No. 3	2-2-50	No. 7	2-4-50		
No. 4	2-2.5-50	No. 8	2-4.5-50		

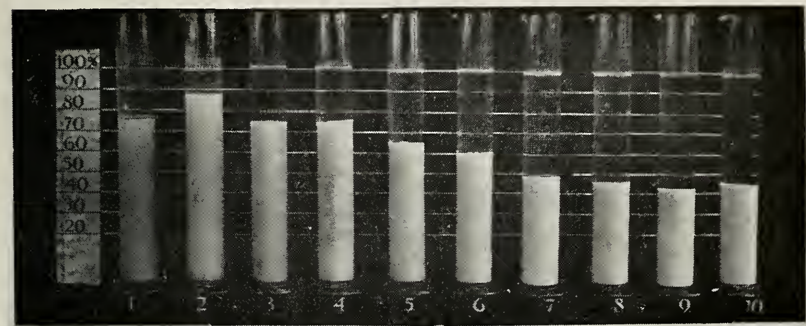

FIG. 4 -- High calcic hydrate

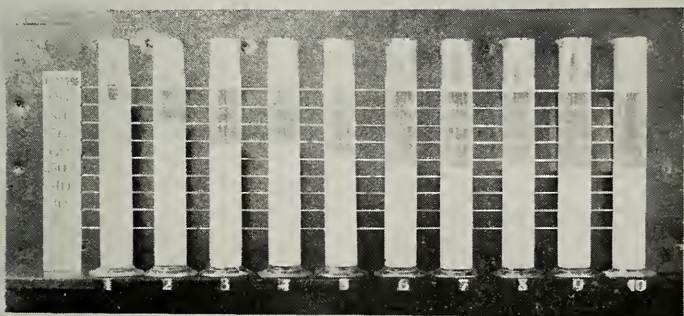

FIG. 5 -- Quicklime

In the 3-pound series, as in Tables 2 and 3, Bordeaux prepared from pulverized copper sulphate and high calcic hydrate gave the highest average suspensions. When low calcic hydrate was used, the highest average suspension occurred in formula 3-3.5-50 and the lowest in 3-1.5-50. The results of using high calcic hydrate show that the highest average suspension occurred in formula 3-1.5-50 and the lowest in 3-6-50. The highest and lowest average suspension occurred in these same formulae when quicklime was used. It may be noted that while Bordeaux 3-1.5-50, prepared from quicklime, showed approximately the same high suspension as that made from high calcic hydrate up to the 2-hour period, after 3 hours the latter had a suspension of 93% while the former showed only 50%. Figures 6 and 7 show the higher suspension of Bordeaux prepared from high calcic lime than from quicklime after 2 hours.

TABLE 4—*Comparison of suspension percentages of Bordeaux mixture prepared from three (3) pounds of copper sulphate and different quantities and forms of lime at ½, 1, 1½, 2, and 3-hour intervals*

No.	Formula	Copper Sulphate	Lime	½ hr.	1 hr.	1½ hrs.	2 hrs.	3 hrs.
		(1) Pulv.	Low Calc. Hydrate	90.0%	70.0%	57.0%	49.0%	43.0%
1.	3-1.5-50	(2) Pulv.	High Calc. Hydrate	99.0	98.0	97.0	96.0	93.0
		(3) Lump	Quicklime	99.0	98.0	94.0	83.0	50.0
		(1) Pulv.	Low Calc. Hydrate	98.0	91.0	83.0	75.0	67.0
2.	3-2-50	(2) Pulv.	High Calc. Hydrate	99.0	98.0	97.0	95.0	92.0
		(3) Lump	Quicklime	99.0	98.0	94.0	81.0	50.0
		(1) Pulv.	Low Calc. Hydrate	98.0	96.0	93.0	86.0	79.0
3.	3-2.5-50	(2) Pulv.	High Calc. Hydrate	99.0	98.0	96.0	95.0	91.0
		(3) Lump	Quicklime	99.0	98.0	94.0	81.0	52.0
		(1) Pulv.	Low Calc. Hydrate	98.0	97.0	94.0	92.0	88.0
4.	3-3-50	(2) Pulv.	High Calc. Hydrate	99.0	97.0	96.0	95.0	90.0
		(3) Lump	Quicklime	98.0	97.0	91.0	78.0	51.0
		(1) Pulv.	Low Calc. Hydrate	99.0	97.0	95.0	92.0	87.0
5.	3-3.5-50	(2) Pulv.	High Calc. Hydrate	99.0	98.0	96.0	93.0	89.0
		(3) Lump	Quicklime	99.0	97.0	92.0	79.0	50.0
		(1) Pulv.	Low Calc. Hydrate	99.0	97.0	94.0	91.0	84.0
6.	3-4-50	(2) Pulv.	High Calc. Hydrate	99.0	98.0	96.0	93.0	85.0
		(3) Lump	Quicklime	98.0	97.0	93.0	77.0	52.0
		(1) Pulv.	Low Calc. Hydrate	98.0	96.0	94.0	91.0	81.0
7.	3-4.5-50	(2) Pulv.	High Calc. Hydrate	99.0	97.0	96.0	93.0	85.0
		(3) Lump	Quicklime	98.0	97.0	90.0	74.0	51.0
		(1) Pulv.	Low Calc. Hydrate	99.0	97.0	94.0	91.0	79.0
8.	3-5-50	(2) Pulv.	High Calc. Hydrate	99.0	97.0	95.0	91.0	82.0
		(3) Lump	Quicklime	98.0	97.0	90.0	73.0	48.0
		(1) Pulv.	Low Calc. Hydrate	98.0	96.0	93.0	90.0	79.0
9.	3-5.5-50	(2) Pulv.	High Calc. Hydrate	99.0	97.0	95.0	91.0	81.0
		(3) Lump	Quicklime	97.0	96.0	81.0	66.0	45.0
		(1) Pulv.	Low Calc. Hydrate	98.0	96.0	93.0	88.0	73.0
10.	3-6-50	(2) Pulv.	High Calc. Hydrate	98.0	97.0	94.0	90.0	81.0
		(3) Lump	Quicklime	97.0	96.0	82.0	67.0	44.0

When low calcic hydrate was used, the highest average suspension occurred in formulae 4-4.5-50, 4-5-50, and 4-5.5-50, there being no significant difference between them. The lowest suspension occurred in formula 4-2-50. When high calcic hydrate was used the highest average suspension occurred in formulae 4-3-50 and 4-3.5-50 and the lowest in formula 4-8-50. The highest suspension recorded for any of the 45 formulae tested was for formula 4-3-50, prepared from high calcic hydrate. The average suspension after one-half hour was 99% and after three hours it was 93%. This particular test produced the finest individual batch of Bordeaux in these experiments. The highest suspension when quicklime was used in this series occurred in formulae 4-3.5-50 and 4-4-50 and the lowest in 4-8-50. See Figures 8 and 9.

Since a high suspension percentage is desirable in Bordeaux mixture it is timely at this point to indicate the formulae in all four series which gave the highest suspension together with the forms of lime and bluestone used. In the 1-pound series the highest suspension occurred in formula 1-1-50, prepared from pulverized bluestone and high calcic hydrate; in the 2-pound series the highest suspension occurred in formula 2-1.5-50, prepared from pulverized bluestone and high calcic hydrate; in the 3-pound series the highest suspension occurred in formula 3-1.5-50, prepared from pulverized bluestone and high calcic hydrate; in the 4-pound series the highest suspension occurred in formula 4-3-50, prepared from pulverized bluestone and high calcic hydrate. It is significant that the Bordeaux mixtures of highest suspension in each of the four series were prepared from pulverized bluestone and high calcic hydrate, the materials that are used in making Instant Bordeaux.

FIGURES 6 and 7

Suspension tests of ten formulae of Bordeaux prepared from high calcic hydrate and quicklime, after two hours.

No. 1	3-1.5-50	No. 6	3-4-50
No. 2	3-2-50	No. 7	3-4.5-50
No. 3	3-2.5-50	No. 8	3-5-50
No. 4	3-3-50	No. 9	3-5 5-50
No. 5	3-3.5-50	No. 10	3-6-50

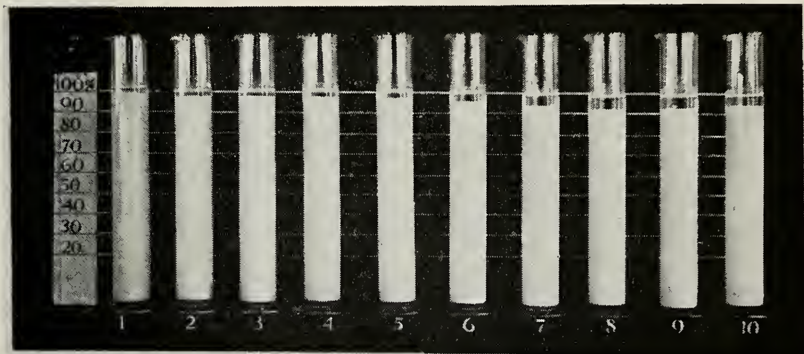

FIG. 6 -- High calcic hydrate

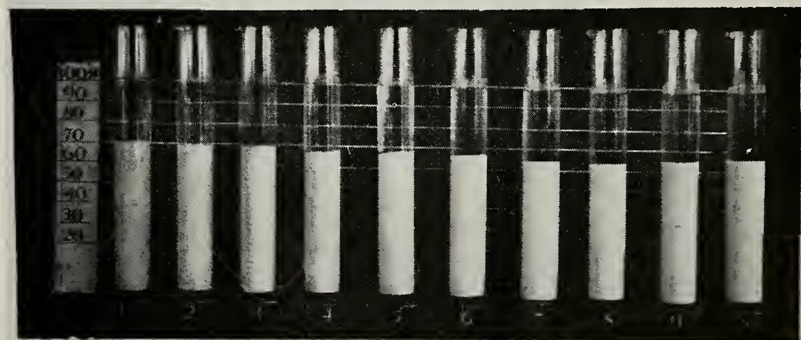

FIG. 7 -- Quicklime

THE EFFECT OF AGE OF MILK-OF-LIME ON BORDEAUX-MIXTURE SUSPENSION

It frequently happens in orchard practice that a surplus of milk-of-lime is prepared for a certain spray application. This material is carried over in suitable containers for use in the next spray, which occurs on an average of 12 days later. Holland has advised soaking hydrated lime before using it for making Bordeaux mixture in order to assure complete wetting of the lime particles.

TABLE 5—*Comparison of suspension percentages of Bordeaux mixture prepared from four (4) pounds of copper sulphate and different quantities and forms of lime at ½, 1, 1½, 2, and 3-hour intervals*

No.	Formula	Copper Sulphate	Lime	½ hr.	1 hr.	1½ hrs.	2 hrs.	3 hrs.
		(1) Pulv.	Low Calc. Hydrate	73.0%	60.0%	48.0%	43.0%	39.0%
1.	4-2-50	(2) Pulv.	High Calc. Hydrate	99.0	98.0	97.0	96.0	93.0
		(3) Lump	Quicklime	99.0	98.0	96.0	89.0	76.0
		(1) Pulv.	Low Calc. Hydrate	95.0	87.0	65.0	56.0	51.0
2.	4-2.5-50	(2) Pulv.	High Calc. Hydrate	99.0	99.0	97.0	96.0	94.0
		(3) Lump	Quicklime	99.0	98.0	97.0	91.0	77.0
		(1) Pulv.	Low Calc. Hydrate	98.0	96.0	85.0	72.0	59.0
3.	4-3-50	(2) Pulv.	High Calc. Hydrate	99.0	99.0	97.0	96.0	93.0
		(3) Lump	Quicklime	99.0	98.0	96.0	92.0	77.0
		(1) Pulv.	Low Calc. Hydrate	98.0	97.0	95.0	92.0	85.0
4.	4-3.5-50	(2) Pulv.	High Calc. Hydrate	99.0	98.0	96.0	96.0	92.0
		(3) Lump	Quicklime	99.0	98.0	96.0	90.0	76.0
		(1) Pulv.	Low Calc. Hydrate	99.0	97.0	95.0	93.0	88.0
5.	4-4-50	(2) Pulv.	High Calc. Hydrate	99.0	98.0	97.0	96.0	91.0
		(3) Lump	Quicklime	99.0	97.0	96.0	91.0	75.0
		(1) Pulv.	Low Calc. Hydrate	99.0	98.0	95.0	93.0	85.0
6.	4-4.5-50	(2) Pulv.	High Calc. Hydrate	99.0	98.0	96.0	95.0	90.0
		(3) Lump	Quicklime	98.0	95.0	96.0	90.0	76.0
		(1) Pulv.	Low Calc. Hydrate	99.0	98.0	95.0	93.0	84.0
7.	4-5-50	(2) Pulv.	High Calc. Hydrate	99.0	98.0	97.0	95.0	89.0
		(3) Lump	Quicklime	98.0	97.0	94.0	90.0	75.0
		(1) Pulv.	Low Calc. Hydrate	99.0	98.0	95.0	93.0	84.0
8.	4-5.5-50	(2) Pulv.	High Calc. Hydrate	99.0	98.0	96.0	95.0	90.0
		(3) Lump	Quicklime	98.0	97.0	94.0	90.0	76.0
		(1) Pulv.	Low Calc. Hydrate	98.0	97.0	95.0	92.0	83.0
9.	4-6-50	(2) Pulv.	High Calc. Hydrate	99.0	98.0	95.0	94.0	87.0
		(3) Lump	Quicklime	98.0	96.0	93.0	89.0	74.0
		(1) Pulv.	Low Calc. Hydrate	99.0	98.0	96.0	93.0	84.0
10.	4-6.5-50	(2) Pulv.	High Calc. Hydrate	99.0	97.0	96.0	94.0	88.0
		(3) Lump	Quicklime	99.0	96.0	94.0	89.0	73.0
		(1) Pulv.	Low Calc. Hydrate	99.0	98.0	95.0	93.0	84.0
11.	4-7-50	(2) Pulv.	High Calc. Hydrate	99.0	97.0	96.0	95.0	90.0
		(3) Lump	Quicklime	98.0	95.0	92.0	88.0	72.0
		(1) Pulv.	Low Calc. Hydrate	99.0	98.0	95.0	93.0	84.0
12.	4-7.5-50	(2) Pulv.	High Calc. Hydrate	99.0	97.0	95.0	93.0	88.0
		(3) Lump	Quicklime	96.0	93.0	90.0	85.0	71.0
		(1) Pulv.	Low Calc. Hydrate	99.0	98.0	95.0	92.0	82.0
13.	4-8-50	(2) Pulv.	High Calc. Hydrate	98.0	97.0	94.0	92.0	87.0
		(3) Lump	Quicklime	96.0	94.0	91.0	86.0	70.0

In Table 6 are given the effects on suspension of aging milk-of-lime made from both quicklime and high calcic hydrate.

The percentages above are the averages of five tests. For both the quicklime and the high calcic hydrate, the fresh and the 15-day-old milk-of-lime were made from the same original batches respectively. These data indicate no wide difference in suspension of the fresh and 15-day-old milk-of-lime made from high calcic hydrate. There was a slightly higher suspension when fresh lime was used, and there was a significant decrease in suspension in the case of the 15-day-old quicklime at the 3-hour period.

The high calcic hydrate Bordeaux made from both the fresh and 15-day-old milk-of-lime showed more uniformity and higher suspension than the quicklime, especially after three hours, when the difference in the suspension of the Bordeaux made from quicklime of different age was 10% compared with 1% for the high calcic hydrate.

Figures 10 and 11 show the suspension percentages of Bordeaux mixture resulting from the use of fresh and of 15-day-old milk-of-lime prepared from high calcic hydrate and from quicklime.

FIGURES 8 and 9

Comparison of suspension in ten formulae of Bordeaux prepared from high calcic hydrate and from quicklime after 1 hour.

No. 1	4-2-50	No. 6	4-4.5-50
No. 2	4-2.5-50	No. 7	4-5-50
No. 3	4-3-50	No 8	4-5.5-50
No. 4	4-3.5-50	No. 9	4-6-50
No. 5	4-4-50	No. 10	4-6.5-50

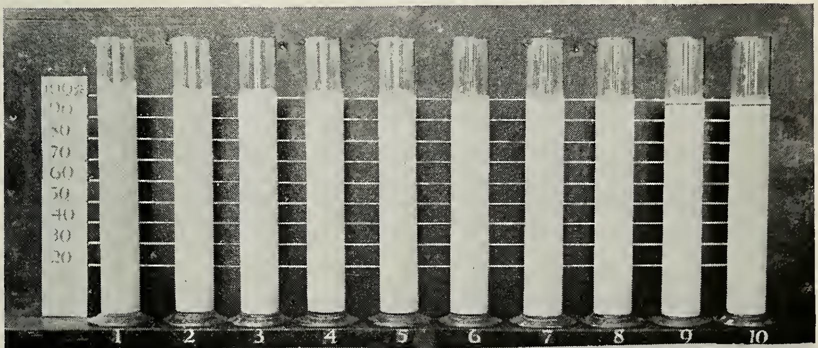

FIG. 8 -- High calcic hydrate

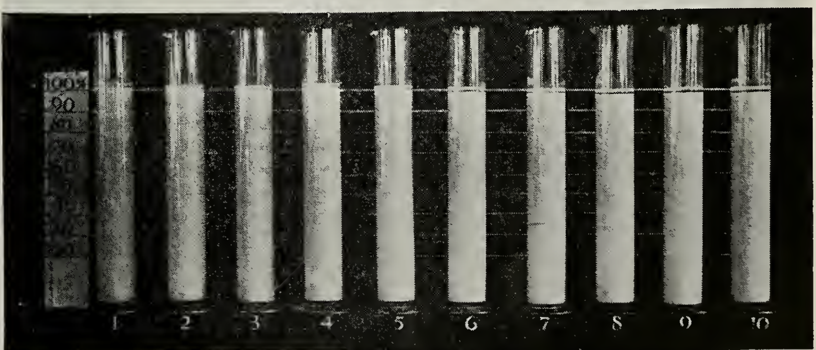

FIG. 9 -- Quicklime

TABLE 6—*The effect of using 15-day-old milk-of-lime and fresh milk-of-lime prepared from quicklime and high calcic hydrate on the suspension of the resulting 4-4-50 Bordeaux mixtures (Temperature at mixing, 14°C.)*

Milk-of-lime source	Age of milk-of-lime	1 hour	2 hours	3 hours
Quicklime	Fresh	98.0%	96.0%	86.0%
High calcic Hydrate	Fresh	99.0	97.0	96.0
Quicklime	15 days old	98.0	95.0	76.0
High calcic Hydrate	15 days old	99.0	98.0	95.0

FIGURES 10 and 11

The effect of age of milk-of-lime prepared from high calcic hydrate and quicklime on the suspension of Bordeaux mixture 4-4-50 after 3 hours.

Nos. 1, 2, 3, 4, 5 — 15-day old milk-of-lime
Nos. 6, 7, 8, 9, 10 — Fresh milk-of-lime

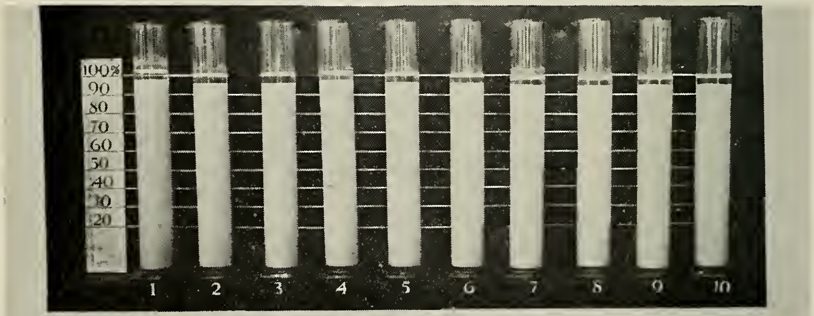

FIG. 10 -- Bordeaux prepared from high calcic hydrate

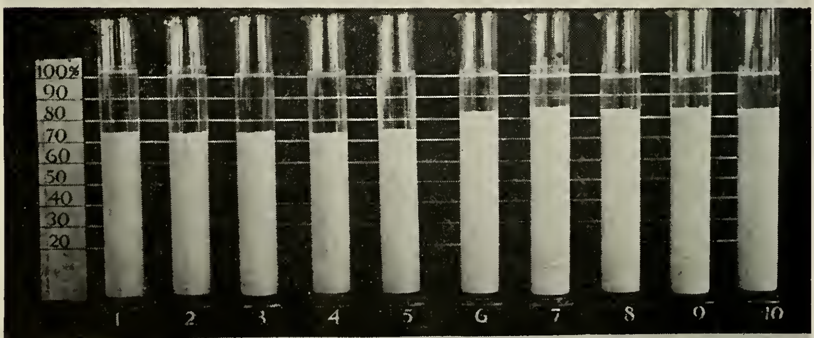

FIG. 11 -- Bordeaux prepared from quicklime

Decomposition of Bordeaux Mixture and the Formation of Spherulites

The settling of Bordeaux mixture is caused by a change in its colloidal condition. When settling has progressed to a point where the suspension is approximately 25% of the original, the change in the colloidal nature of Bordeaux mixture is accompanied by a crystallization of part of the suspended material. Bordeaux decomposition probably begins immediately after mixing, but visible changes in chemical composition begin with the formation of crystals, which is accompanied by a change in color from cobalt blue to directoire blue.

The main bulk of deteriorated Bordeaux is made up of various types of crystals, the most of which have been designated by various authors as "sphaero-crystals." This terminology is probably faulty, because the inference is that these microscopic spherical bodies are individual crystals. This is not the case, however, as an examination with a petrographical microscope will reveal. The light-blue spherical bodies are aggregates of very minute crystals radiating from a common center. Instead of the designation "sphaero-crystals," the term "spherulites" is more accurately descriptive of these small bodies.

The spherulites formed in Bordeaux mixture vary in size from 1 to 40 microns, depending upon their age Since they "grow", the larger spherulites occur in the older samples. It is probable that the individual crystals of which the spherulite is the aggregate belong to the orthorhombic system, but they are far too small for satisfactory determination of optical properties. According to the reaction which is supposed to occur when copper sulphate and lime are mixed in water this blue substance of the spherulite is a basic copper sulphate, or possibly, in part, a basic sulphate of copper and lime.

The factors known to influence the rapidity of crystallization of Bordeaux according to Butler *(2)* are concentration of copper sulphate, ratio of copper sulphate to CaO, and temperature. The correlation of the first two factors is indicated by the fact that crystallization does not occur when the copper sulphate content is less than 0 25% and the ratio of copper sulphate to CaO is 1:0.5. When this ratio is widened to 1:0.25, no crystallization occurs even when the copper sulphate content is 2%. Bordeaux of a high copper-sulphate content (2 to 6%) crystallizes more slowly than Bordeaux of lower content. Crystallization is hastened by a rise in temperature regardless of the concentration of copper sulphate or the ratio between it and CaO in the mixture. It was found that Bordeaux containing 4% copper sulphate and equal parts of copper sulphate and CaO crystallized and deteriorated after 144 hours at 9°C., while at 25°C. deterioration occurred after only 16 hours. To the factors just mentioned may be added the use of supplementary materials that function as colloid stabilizers, which will be described later.

According to Holland and associates *(10)* "the decomposition of

Bordeaux mixture is manifested by a gradual loss of gelatinous character, more rapid settling, spurting of the mixture, and the slow acquisition of a purplish color. The final dense aggregates are said to be sphaero-crystals.''

In the present study no significant difference in the time of first appearance of spherulites was observed in Bordeaux prepared from pulverized copper sulphate and high calcic hydrate and that prepared from stock solutions of lump copper sulphate and quicklime. At temperatures ranging between 23 and 25°C. it was found that 4-4-50 Bordeaux mixture prepared from high calcic hydrate and from quicklime (both limes having been made from the same limestone) developed spherulites after standing in uncovered 500 c.c. graduates for 7½ hours. Slight heating of 4-4-50 Bordeaux mixture, followed by slow cooling, induced the formation of spherulites immediately after its preparation.

The work of Holland and associates *(11)* shows that various substances added to Bordeaux mixture prolong suspension. Among the substances which gave the best results were bentonite, wilkinite, tannic acid, sugar, and wheat flour. In the present study of spherulite formation, bentonite, tannic acid, and sugar were added to 4-4-50 Bordeaux mixture. The data in the following table indicate the results obtained.

TABLE 7—*The effect of adding supplementary materials to* 4-4-50 *Bordeaux mixture on the formation of spherulites*

No.	Material added		First appearance of spherulites	Maximum spherulite formation	Temperature
1	Bentonite	0.5%	10 hours	27 hours	23-25°C.
2	Bentonite	1.0%	20 hours	35 hours	same
3	Bentonite	1.5%	36 hours	48 hours	same
4	Tannic Acid	0.5%		None*—15 days	same
5	Sugar	0.5%		None*—15 days	same
6	Check		7½ hours	24 hours	same

*Earlier than 15 days.

The data show that all the supplementary materials retarded the formation of spherulites. A difference of 1% in the quantity of bentonite had the effect of retarding initial spherulite formation by 26 hours. It is evident that tannic acid and sugar prevent crystallization of Bordeaux mixture for at least 15 days. Despite the fact that the minimum suspension of the Bordeaux mixture containing tannic acid and sugar was 35% and 44% respectively, there was no evidence of crystallization and deterioration except the change in the gelatinous nature of the samples after 15 days. The questions arise, when, in the process of decomposition, does Bordeaux mixture cease to be such, and when does decomposition actually begin? When crystallization is complete, the purplish residue has none of the characteristics of Bordeaux and cannot, therefore, be so designated.

The color of 4-4-50 Bordeaux mixture freshly made is sevres blue, according to the color charts of Maerz and Paul *(14)* (K-9, Plate 33). The color of the sample to which sugar was added was the same as the check. The addition of 0.5% of tannic acid changed the color to kara green (Z-1, Plate 38). When the maximum crystallization of 4-4-50

Bordeaux has occurred, the residue appears to be a heavy and finely pulverulent substance of directoire blue color. The addition of 0.5% of bentonite did not cause an appreciable change, but 1.5% of this material caused a grayish blue (J-7, Plate 33).

The inference from the foregoing data is that small quantities of sugar and bentonite may aid in preserving Bordeaux mixture. The use of sugar in Bordeaux has been practiced for a long time; bentonite, however, has only recently been used as a sticker with certain proprietary spray materials. For this purpose it would be unnecessary in Bordeaux mixture, which has, itself, excellent sticking properties. Furthermore, bentonite added to Bordeaux would increase the solid material in the fungicide, which is undesirable.

Color of Bordeaux Mixture

The use of color as an indicator of the quality of Bordeaux has been emphasized by different investigators. From the standpoint of accurate description, the color terminology found in the literature on this subject has been loose and at times meaningless. We find such expressions as light blue, full blue, deep blue, etc. According to Maerz and Paul *(14)* "the name blue in fact is meaningless, except within wide limits, unless the influencing side color is specified." In this dictionary of color are found more than a thousand shades of blue, most of which have no word description. One way to identify such a large number of intergrading shades of one basic color is to use a numerical system. Spectroscopic measurements in terms of reflected light of various wave lengths would probably be an improvement over the numerical system.

Color determinations of certain formulae of Bordeaux mixture were attempted in this study. It was soon discovered that no two formulae were of the same color, and furthermore, because of the limitation of the color charts used, no accurate description of color was possible. However, such color descriptions as are herein made are probably more accurate than the use of "deep blue", "full blue", and "dark blue".

In Table 8 is found a color description of 22 formulae of Bordeaux mixture, half of which were prepared from stock solutions of copper sulphate and quicklime and half from pulverized copper sulphate and high calcic hydrate. The scheme followed was to determine the color of the Bordeaux containing the smallest concentration of lime, the lowest suspension, and the highest suspension. Color determinations were made immediately after the Bordeaux was mixed. The color determinations in this table indicate that the formulae of the 1 and 2-pound series with the highest suspensions are of a lighter shade of blue than of highest suspensions in the 3 and 4-pound series. This may indicate that there is a correlation between color and concentration in formulae showing maximum suspensions.

TABLE 8—*The color of Bordeaux mixture prepared from different forms and amounts of copper sulphate and lime, identified by means of color chart in "Dictionary of Color" (23)*

Kind of Bordeaux mixture	Formula	Why selected	Numerical Designation	Color name
Instant Bordeaux prepared from pulverized copper sulphate and high calcic hydrate	1-0.5-50	Lowest lime content	34-L-2*	Grotto blue
	1-1.-50	Highest suspension	34-K-3	Betw. Grotto blue and blue Jewel
	1-5.50	Lowest suspension	33-J-2	Calamine blue
	2-1.-50	Lowest lime content	33-K-2	Beryl
	2-1.5-50	Highest suspension	34-K-3	Next to Blue Jewel
	2-5.5-50	Lowest suspension	34-G-3	Next to Light blue 6[T]
	3-1.5-50	Lowest lime content, highest suspension	33-L-7	Nearly Cobalt blue[P]
	3-6.-50	Lowest suspension	33-J-6	Next to Airway
	4-2.-50	Lowest lime content	33-L-6	Nearly Cobalt blue[P]
	4-3.-50	Highest suspension	33-K-10	Nearly Sevres
	4-8.-50	Lowest suspension	33-I-7	Next to Daphne
Bordeaux mixture prepared from stock solutions of copper sulphate and quicklime	1-0.5-50	Lowest lime content	34-L-4	Blue Jewel
	1-1.5-50	Highest suspension	33-J-3	Next to Calamine blue
	1-5.-50	Lowest suspension	33-F-3	Lighter than Beryl blue
	2-1.-50	Lowest lime content Highest suspension	33-L-7	Nearly Cobalt blue[P]
	2-5.5-50	Lowest suspension	33-I-4	Lighter than Italian blue
	3-1.5-50	Lowest lime content, highest suspension	34-K-7	Louis Philippe
	3-6.-50	Lowest suspension	33-I-6	Airway
	4-2.-50	Lowest lime content	33-L-9	Close to Sevres
	4-3.-50	Highest suspension	33-K-7	Nearly Cobalt blue
	4-7.5-50	Lowest suspension	33-I-6	Airway

*34-L-2 means Chart 34, L horizontal, 2 vertical.

In Table 9 are found color determinations of Bordeaux of 13 formulae having a constant copper-sulphate content of 4 pounds and different quantities of high calcic hydrate as indicated in the table. The color description in this table includes most of the formulae of Bordeaux of the 4-pound series commonly used for spraying. An increase in the lime content is accompanied by lighter shades of blue, which would be expected.

TABLE 9—*The color of 13 different formulae of Bordeaux prepared from four pounds of pulverized copper sulphate and varying quantities of high calcic hydrate*

Formula	Description	Color Name
4-2.0-50	33-L-6	Close to Cobalt Blue
4-2.5-50	33-L-8	Close to Cobalt Blue
4-3.0-50	33-K-10	Close to Sevres
4-3.5-50	33-K-9	Close to Sevres
4-4.0-50	33-K-9	Close to Sevres
4-4.5-50	33-K-8	Close to Louis Philippe
4-5.0-50	33-K-7	Close to Louis Philippe
4-5.5-50	33-K-6	Close to Watteau
4-6.0-50	33-J-7	Close to Watteau
4-6.5-50	33-J-7	Close to Watteau
4-7.0-50	33-J-7	Close to Watteau
4-7.5-50	33-I-7	Close to Dresden Blue
4-8.0-50	33-I-7	Close to Dresden Blue

The Effect of Arsenical Compounds and Supplementary Materials on the Suspension of Bordeaux

In orchard and garden spraying, Bordeaux mixture is frequently used in combination with arsenicals in the form of lead, calcium, and magnesium arsenate. The effect of adding these compounds on the suspension of Bordeaux mixture 4-4-50 is shown by the figures in Table 10. These figures show the average of six suspension tests. In these tests the dry arsenates were added after the Bordeaux had been mixed and thoroughly stirred and before pouring it into the graduate. There was no significant difference in suspension after one hour.

Table 10—*The effect of adding lead, calcium, and magnesium arsenate on the suspension of* 4-4-50 *Bordeaux mixture.* (*Temperature,* 19°C.)

No.	Material added	1 hr. Suspension	2 hrs. Suspension	3 hrs. Suspension
1.	Lead arsenate 3 lbs per 100 gal.	98.0%	96.0%	94.0%
2.	Calcium arsenate 2½ lbs. per 100 gal.	97.0	95.0	92.0
3.	Magnesium arsenate 2½ lbs. per 100 gal.	97.0	95.0	92.0
4.	Check	98.0	96.0	94.0

At the end of three hours, arsenate of lead showed no effect on suspension while calcium and magnesium arsenate decreased suspension only 2 percent, which is not significant.

In Table 7 the effect of adding sugar, bentonite, and tannic acid as preservaties of Bordeaux is shown.

It has been determined by a number of investigators that sugar and molasses in small amounts have a beneficial effect on the preservation of Bordeaux mixture. Kelhofer *(13)* suggested the preservation of Bordeaux mixture by the addition of 50 to 100 grams of sugar per hectoliter. He demonstrated that this method of preservation was due not to the dissolving of sugar on the basic copper combination, but to the action of sugar as a colloid stabilizer (Schutzkolloid). Wöber *(28)* points out that the quantity of sugar needed for preservation depends on the excess lime present. Doran *(6)* reports an increase of four times in toxicity to spores of *Venturia inaequalis* as a result of adding 4 pounds of sugar to 50 gallons of 4-2-50 Bordeaux mixture.

In Table 11 the effect of adding bentonite, tannic acid, and sugar on the suspension of 2-2-50 and 4-4-50 Bordeaux mixture is shown.

An increase in suspension followed the addition of all supplements except in the 2-pound series, when 0.5% of bentonite was used. No explanation for this decrease in suspension is attempted. In this particular test there was a distinct separation of the Bordeaux precipitate, the mother liquor appearing in irregular patches throughout the container. This characteristic disappeared after 8 hours. The best results in the 2 pound series followed the addition of tannic acid and 1.5% of bentonite, while in the 4-pound series 1.0 and 1.5% of bentonite gave the best suspension, particularly after 4 hours. The data seem to indicate that supplements have more effect on the 4-pound than on the 2-pound series.

TABLE 11—*The effect on its suspension of adding supplementary materials for Bordeaux mixture*

Formula	Supplement		Suspension 1 hr.	Suspension 2 hrs.	Suspension 3 hrs.	Suspension 4 hrs.
2-2-50	Bentonite	0.5%	94.0	77.0	67.0	50.0
2-2-50	Bentonite	1.0	96.0	85.0	79.0	57.0
2-2-50	Bentonite	1.5	96.0	86.0	77.0	58.0
2-2-50	Tannic acid	0.5	96.0	93.0	89.0	86.0
2-2-50	Sugar	0.5	95.0	86.0	77.0	70.0
2-2-50	Check		92.0	85.0	78.0	45.0
4-4-50	Bentonite	0.5	98.0	92.0	77.0	75.0
4-4-50	Bentonite	1.0	98.0	94.0	86.0	82.0
4-4-50	Bentonite	1.5	98.0	96.0	94.0	91.0
4-4-50	Tannic acid	0.5	97.0	94.0	82.0	76.0
4-4-50	Sugar	0.5	97.0	91.0	77.0	73.0
4-4-50	Check		96.0	80.0	70.0	60.0

SUMMARY

This investigation deals largely with suspension tests of Bordeaux mixture prepared in various ways and from different forms and quantities of copper sulphate and lime. The data resulting from testing Bordeaux mixture of 43 formulae indicate that Instant Bordeaux prepared from pulverized copper sulphate and high calcic hydrate gave higher average suspensions than Bordeaux mixture prepared from stock solutions of copper sulphate and quicklime or from low calcic hydrate.

Judged by its dispersion as indicated by numerous suspension tests, chemical hydrated lime is comparable in activity to quicklime, both limes originating from the same limestone. The uniformity, extreme fineness, and high calcium oxide content of chemical hydrated lime commend it for making Bordeaux mixture.

Freshly-prepared milk-of-lime gave slightly higher suspension in 4-4-50 Bordeaux mixture than 15-day-old milk-of-lime. The suspension percentages after three hours when fresh milk-of-lime was prepared from quicklime and from chemical hydrated lime were respectively 86 and 96 as compared with 76 and 95, when 15-day-old milk-of-lime was used.

Spherulites are aggregates of minute crystals formed in the process of decomposition of Bordeaux mixture. Their composition is unknown at present. They vary in size from 1 to 40 microns. At temperatures from 23° to 25° C. the first appearance of spherulites in Bordeaux mixture 4-4-50 occurred after 7½ hours. The addition of 1.5% of bentonite delayed the formation of spherulites 28.5 hours. Spherulites did not form in 15 days when 0.5% of sugar or 0.5% of tannic acid was added to Bordeaux 4-4-50 formula.

Color is generally considered to be one of the indicators of the quality of Bordeaux mixture. Color determinations of Bordeaux mix-

ture of 23 formulae by means of color charts indicate that no two different formulae of Bordeaux mixture are identical in color.

Highest suspension, as in formula 3-1.5-50, has been correlated with the deepest shades of blue (cobalt blue). Bordeaux mixture of low copper sulphate concentration and high suspension, such as formulae 1-1-50 and 2-1.5-50, have a lighter shade of blue (grotto-blue jewel) than those of higher concentration and high suspension, such as 3-1.5-50 and 4-3-50, in which the color closely resembles cobalt blue or sevres. Color can be expressed more accurately than in such terms as light blue, dark blue, or full blue by using the nominal or numerical description.

The addition of lead arsenate, 3 pounds per 100 gallons, and of magnesium and calcium arsenate, 2½ pounds per 100 gallons, caused no significant change in the suspension of Bordeaux 4-4-50. The addition of bentonite, tannic acid, or sugar aided the suspension of 4-4-50 Bordeaux after 3 hours.

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