THESIS

Physical Structure of

Spraying Substances

F. W. Owen

1902

T H E   P H Y S I C A L   S T R U C T U R E

O F

S P R A Y I N G   S U B S T A N C E S.

T H E S I S.

By

Floyd W. Owen,

M. A. C.   Class '02.

THESIS

103217

THE PHYSICAL STRUCTURE

OF

SPRAYING SUBSTANCES.

By

Floyd W. Owen.

Spraying consists in covering plants, or parts of plants, with a thin uniform film of liquid capable of destroying or preventing an attack of some particular parasitic organism. A spraying substance must possess poisonous, caustic or offensive qualities and should possess a suitable physical structure. The first named properties have received much attention; the last named have received little or none. The object of this study is to discover the most suitable physical structure of one class of spraying substances--the arsenites.

More definitely the materials with which I have worked are: White arsenic, Paris green, pure arsenite of lime, London purple, and a few arsenoids. The method of work with each was:--To examine the physical structure under a compound microscope; to measure the diameter of the particles with a micro-millimeter scale; and to determine the time of suspension in water. In the case of the arsenoids, chemical analyses for white arsenic were also made. In testing the times of suspension, 1.25 grs.

of an average sample of the material to be tested was added to 25 cc of water in a tall graduate. After vigorous shaking, the mixture was allowed to rest until all of the sediment had reached the bottom, the time required then being noted. Several ordinary samples of each substance were examined in the ways mentioned, and by repeating tests of each one, quite accurate comparisons were obtained. Samples of white arsenic and paris green were pulverized in a glass mortar, in order to compare the time of suspension of the smaller particles with that of the ordinary material.

An inquiry as to the relation existing between the diameters of small particles and their times of suspension, brought the following from the U. S. Department of Agriculture, Division of Soils:

"The theoretical rate of settling of small particles of spherical form in water would be, with the conditions the same, directly as the radii of the particles. You will see that this would follow from the fact that the mass varies as the cube of the radius, while the effective surface--in this case the cross-section of the sphere through the center--varies as the square of the radius. Consequently, if one particle was twice the diameter of the second, it would settle twice as fast. This relation does not hold, however, for irregular particles and it has not been possible to obtain a definite relation between the mean diameter of the particles and the rate of settling.

of an average sample of the material to be tested was added to 25 cc of water in a tall graduate. After vigorous shaking, the mixture was allowed to rest until all of the sediment had reached the bottom, the time required then being noted. Several ordinary samples of each substance were examined in the ways mentioned, and by repeating tests of each one, quite accurate comparisons were obtained. Samples of white arsenic and paris green were pulverized in a glass mortar, in order to compare the time of suspension of the smaller particles with that of the ordinary material.

An inquiry as to the relation existing between the diameters of small particles and their times of suspension, brought the following from the U. S. Department of Agriculture, Division of Soils:

"The theoretical rate of settling of small particles of spherical form in water would be, with the conditions the same, directly as the radii of the particles. You will see that this would follow from the fact that the mass varies as the cube of the radius, while the effective surface--in this case the cross-section of the sphere through the center--varies as the square of the radius. Consequently, if one particle was twice the diameter of the second, it would settle twice as fast. This relation does not hold, however, for irregular particles and it has not been possible to obtain a definite relation between the mean diameter of the particles and the rate of settling.

the variations in surface conditions is undoubtedly largely responsible for the irregularities that are observed."

W H I T E A R S E N I C.

This ordinarily occurs as a clear, white, tasteless, odorless powder, slightly soluble in water and composed of small octahedral crystals whose chemical composition is As_2O_3. Under the microscope, I found the particles to be of variable forms and sizes; to have a semi-transparent appearance; and to range in their diameters from 0.0033 mm. to 0.033 mm., the average being 0.0266 mm. The suspension of an ordinary sample tested as above described, was three minutes; of a pulverized sample, 5.5 to 6 minutes.

P A R I S G R E E N.

Under the microscope, Paris green was found to be composed of small, quite uniform green spheres with a diameter ranging from 0.013 mm. to 0.023 mm. Of ten samples which I examined, all contained a quantity of small, semi-transparent particles, a small portion of which was impurity. In a few samples crystals of free white arsenic could be distinguished, though the microscope was not found to be reliable in determining very accurately whether the amount was injurious or not.

A microscopic comparison of lime and the impurity found in most of the arsenites indicated that free lime was frequently present. There was also often seen particles of a very finely divided material which did not resemble Paris green spheres, and yet may be a form of aceto-arsenite of copper in which the chemical action was not quite complete. This is easily mistaken for impurity.

Aside from a chemical analysis--really the only conclusive test--the most satisfactory method proved to be the compound microscope which almost certainly decided a sample to be pure or adulterated, and with some experience, an approximate estimation of the quantity and quality of the impurity could be made. By this means crystals of water- soluble arsenic were detected, and anything not pure Paris green was readily seen. Different lots of this substance, however, were found to vary a great deal in their structure, so that the size of the spheres was never the same, and yet, uniformity to a high degree in any one sample can be expected.

The suspension of the ten samples was examined in the way indicated and found to vary from 3.5 to 4 minutes; of a sample pulverized to a condition in which the color was midway between white and the green of the ordinary substance--the particles averaging half the diameter of those of the original material--the time was 6.5 to 7 minutes. One great fault of Paris green is its short time of suspension, and were it necessary, the material could be pulverized in a mill, thereby losing its

green color and becoming white. But correspondence with manufacturers indicated that it is not only possible but is much easier for them to make a product of much smaller particles than those of the ordinary size, and that it is only customary to produce the larger crystals--such material having a deeper, richer green, and being, they say, what the trade demands. Such a paris green would certainly possess the advantages of the ordinary, and yet be capable of remaining a longer time in suspension. It would be far easier to apply, and more effective, uniform and economical in its results.

P U R E   A R S E N I T E   O F   L I M E.

Samples of this were made by boiling white arsenic, one part, and unslaked lime, two parts by weight. These were tested by acidifying with hydrocloric acid and then subjecting to hydrogen sulphide, any trace of free arsenic being precipitated as the yellow sulphide of arsenic. From the tests, I found that both should be boiled together and for at least a half hour as the lime in dissolving combines with the arsenic and forms a very poisonous, but insoluble, and so a perfectly safe spraying compound.

A dry sample of the pure arsenite of lime is a fine, grayish white powder, which , microscopically, was seen to be of simple structure, the particles being granular, somewhat transparent, exceedingly variable in size, and irregular in shape. Measurements were found

impracticable. An examination showed its time of suspension to be five minutes.

L O N D O N P U R P L E.

Eight samples of London purple were collected from various dealers, and examined. Highly magnified, the purest sample was seen to consist of irregularly shaped bodies of mostly small though widely different sizes, the surface of the larger particles being rough and uneven. Some had merely a dull purple color, while other masses--under a certain focus--were reddish purple and had a brilliant metallic lustre. All samples contained foreign matter in varying amounts, much of which existed as very fine particles with no resemblance to London purple, but corresponding to some of the impurity found in Paris green. Small, rectangular or stick-shaped bodies which were transparent were also occasionally detected. Measurements proved impracticable.

The suspension of the samples ranged from twelve to fifteen minutes, which fact accounts for the little agitation this substance requires and its consequent ease of application,--the probable explanation of the popularity London purple held for a time regardless of its frequent injury to foliage. The buoyancy of the particles is evidently due to their extraordinary irregularity and large surface for a small bulk, these combined,

providing the material with a floating power.

A R S E N O I D S.

Six of the so-called "Arsenoids", manufactured by the Adler Color and Chemical Works of New York, were examined. The first--"No. 2"--is a whitish green powder. Under the microscope, the particles were very small (some were barely visible) and adherent, forming small masses. Except for the presence of some free arsenic, very little impurity was seen. The suspension of this arsenoid was six minutes. A chemical analysis gave 33.457% of total As_2O_3, the most of which was combined with copper, a small though injurious portion being free.

"No. 3" arsenoid microscopically contained two principle substances. The first consisted of small, transparent, irregularly shaped particles, some of which were granular; the second of dark colored bodies but otherwise like the first. Some crystals resembling those of paris green were also seen and as the chemical examination showed copper to be present, true Paris green was believed to be an ingredient. No free white arsenic was distinguished. The arsenoid's time of suspension was four minutes. An analysis showed only 14.927% of As_2O_3 none of which was free, a quantity of lead, and a trace of copper and bismuth.

Arsenoid "No. 4" had a distinct greenish tinge, and under the microscope, consisted of the same small, irregular particles as the above. Some soluble blue--round blue bodies of variable sizes--and a quantity of green material, evidently Paris green, were noted. This sample remained in suspension six minutes. Chemically it contained 56.491% of total arsenic, some copper, and the most free arsenic of any sample.

Besides the small sized particles above mentioned "No. 5" contained a large amount of Paris green or a similar arsenite of copper. Its time of suspension was the longest of all, being seven minutes. 64.727% of total As_2O_3 were found, entirely too much being free however. Copper was also present.

The last arsenoid , "No. 6", differed from the above only in being of a lighter color, containing less copper and less free arsenic, and having a total content of 63.698% of As_2O_3,--entirely too much of the latter being free. Its time of suspension was 6.5 minutes.

"Green Arsenoid" is a plain arsenite of copper, chemically resembling Paris green except that the acetic acid is eliminated. Microscopically it was found to be a very finely divided material, almost free from foreign matter. Its suspension was eight minutes--more than twice as long as some samples of Paris green.

In conclusion I hope to have shown that the value of

a spraying substance depends somewhat upon its physical structure and the size of its particles, and how much attention this should receive from both manufacturer and sprayer. We are in great need of cheap and reliable arsenites--those made up of very minute particles and having a sufficiency of combined arsenic, a long time of suspension, absolute insolubility in water and a freedom from free arsenic and other impurities.

Lastly I wish to acknowledge many valuable suggestions in the work from Professor U. P. Hedrick of the College.

S U M M A R Y.

I. The physical structure of spraying substances is very important and in great need of improvement.

II. Spraying substances with particles of much finer division would favor:

1. Economy.
   - (a. In the manufacture--especially of Paris green.
   - (b. In original cost to the sprayer.
   - (c. Less bulk required for a given surface to be covered.
   - (d. In application--by lessening the required agitation and trouble from clogged machinery.

2. Effectiveness.
   - (a. Longer suspension insures greater uniformity in strength of film.
   - (b. Smaller particles insure a more complete distribution of poison for a given amount.
   - (c. Smaller particles adhere better to foliage.

N O T E. The physical structure and time of suspension of Bordeaux Mixture made under various conditions was studied but the results were not conclusive.

The following sets forth graphically a comparison of the examination:

Substance	Suspension in min.	Aver. dia. of partic.	Composition: Total As O	Composition: Other ingredients
White arsenic	3.	.0266 mm.	100%	
White Ars pulver.	5.5	Meas. impr.	"	
Paris green	3.5--4	.018 mm.	58.65%	CuO = 31.29; $C_2H_4O_2$ = 10.06%
Paris gr. pulver.	6.5--7	Meas. impr		" "
Arsenite of lime	5.	" "	Cal. arsenite.	
London purple	12.--15.	" "	Cal. ars.	arsenite and residues.
"No. 2" arsenoid	6.	" "	33.45%	Cu.
"No. 3" arsenoid	4.	" "	14.927%	Pb. Cu. Ni.
"No. 4" arsenoid	6.	" "	56.491%	Cu.
"No. 5" arsenoid	7.	" "	64.727%	Cu.
"No. 6" arsenoid	6.5	" "	63.698%	Cu.
"Green arsenoid"	8.	" "		Plain arsenite of copper.