

SOLUBLE ARSENIOS OXIDE IN PARIS GREEN.

PRELIMINARY REPORT.

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Received October 30, 1900.

FOR the past six months, the authors of this article have been engaged in a more or less complete investigation of the arsenical insecticides, and while working with Paris green devoted considerable time to the study of the so-called "soluble or free arsenious oxide," and methods for its determination.

The recent appearance of two articles in this Journal, giving results somewhat different from those obtained by us, has induced us to present some phases of our work in this preliminary report.

Briefly, so much of these articles as has to do with the subject under consideration may be summed up as follows :

In his work on Paris green, J. K. Haywood¹ tried three methods for the determination of soluble arsenic.

1. A quantity of Paris green was weighed on a filter and extracted with cold water. Arsenic trioxide was found in the filtrate after 2 liters of water had been used and the method was abandoned.

2. Portions of 1 gram each were suspended in 500 cc. of water in stoppered flasks and the arsenic trioxide in solution determined every few days. The following table of results is given :

	Time in days.	Arsenic trioxide extracted. Per cent.
Paris green A	2	1.01
" "	4	1.68
" "	8	2.69
" "	11	4.02
" "	14	4.02
" " B	9	3.41
" "	12	4.86
" "	14	4.86

The author says, "It will be seen that this method finally gave constant and very likely correct results."

3. Extraction with water kept at 50° to 60°. The solution was filtered off and replaced by fresh water each day.

¹ This Journal, 22, 768.

Time in days.	Total arsenic trioxide extracted. Per cent.
1	3.41
2	5.55
3	7.11
4	8.28
5	9.54
6	11.10
7	Still gaining

Since publishing the above, Haywood¹ has observed that in applying the second method above, some copper is obtained in the filtrate, indicating either the solubility of Paris green in cold water or its decomposition by that medium. He favors the former view, and to increase the accuracy of the method, determines the copper in solution and deducts the corresponding amount of arsenic trioxide from the total arsenic trioxide in the solution.

"It is of course possible, even probable," he says, "that the arsenious and copper oxides of Paris green do not go into solution in water in the same proportion that they are present in the original compound, but in the present state of our knowledge it seems to be the most plausible assumption that they do."

The second article mentioned is one by E. W. Hilgard.² The author states that a correction based upon the amount of copper in solution cannot be made since the copper and arsenic do not dissolve in the same proportion in which they are present in the original substance. As an illustration he gives an experiment in which cold water was allowed to slowly percolate through a sample of Paris green. After the passage of 2 liters there was no reaction for copper, though the arsenic continued to be extracted even after the fifth liter. No crystals of arsenic trioxide could be detected by the microscope in the residue thus washed, but only fragments of crushed globules.

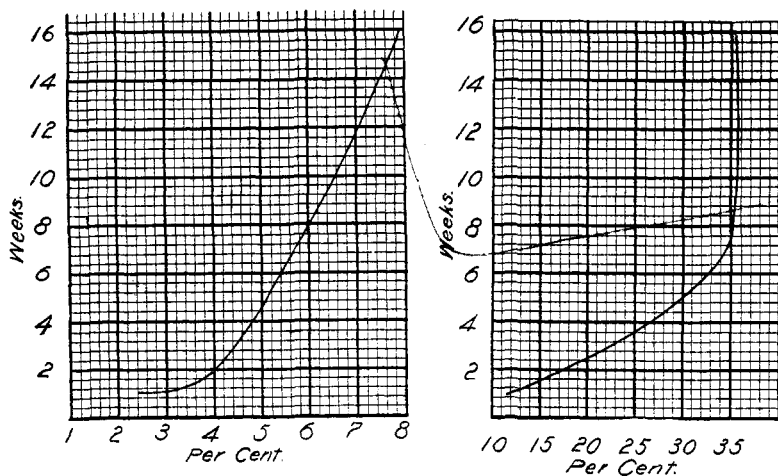
In our work on the subject we used a large number of samples. Several samples of Paris green were made in the laboratory as well as other members of the series containing formic, propionic, and butyric acids, respectively, instead of acetic acid. We studied these as well as many commercial samples of Paris green. We shall confine this report, however, to experiments with one sample which we believe to be nearly pure for the reasons: (1) The

¹ This Journal, 22, 705.

² *Ibid.*, 22, 690.

analysis showed the percentages of cupric oxide and of arsenic trioxide to be nearly in the proportions required by Ehrmann's formula. (2) By treatment with boiling sodium acetate solution according to the method given later in this paper, less than 1 per cent. of arsenic was extracted. (3) The most careful microscopic examination failed to disclose anything but bright spheres of Paris green. (4) The unground sample on standing with water gave off soluble arsenic at a slower rate than any other sample that we have examined.

The sample was divided into two portions: Sample "A" was left in the original condition. In Sample "B" the granules of



Paris green were broken by grinding in a mortar. Several lots of 0.5 gram were weighed from each of these samples and suspended in 500 cc. of distilled water contained in tightly stoppered cylinders. At the end of every two weeks, 250 cc. of the solution were filtered off and titrated with standard iodine. The results of this experiment are plotted in two curves here given, in which the time in weeks is given as ordinates and the percentage of arsenious oxide in solution as abscissas. Owing to the marked difference in the rate of solution, the two curves are not drawn to the same scale.

In Curve "B" there is a gradual increase in soluble arsenic trioxide up to about the end of eight weeks when 35 per

cent. is reached. Beyond this time the increase is slight, being only 0.14 per cent. from the twelfth to the sixteenth week. At this time there was found in the filtrate 5.98 per cent. cupric oxide probably as copper acetate.

Had the copper and arsenious oxides gone into solution in the proportion in which they were present in the original sample, there should have been 19.57 per cent. cupric oxide instead of 5.98 per cent. in solution. It might be urged that the excess of arsenic over copper might be due to uncombined arsenic trioxide in the sample. Such an assumption would require at least 25 per cent. of uncombined arsenic trioxide.

While our results are in harmony with Hilgard's conclusion that copper and arsenic do not dissolve in the proportions in which they exist in Paris green, no close comparison of the experiments can be made as the experiments were made under different conditions. In our work all the products remained in the sphere of action. In Hilgard's work all soluble products were allowed to filter out as fast as formed. His green seems, also, to have been exposed to the action of the air during the percolation.

We believe that the action of water on Paris green is a hydrolytic action. Leaving out of consideration the probable formation of secondary products, it is probable that a small amount of copper acetate (whence the soluble cupric oxide), soluble arsenic trioxide, and basic copper acetate are formed. The reaction seems to take place in accordance with the law of mass action, a state of equilibrium being reached when about 36 per cent. of arsenic trioxide has passed into solution under the conditions previously stated. It is quite likely that all the arsenic could be rendered soluble by replacing the supernatant liquid with fresh water from time to time and allowing to stand for a longer period. In addition to the evidence already cited in support of this view it may also be added that the analysis of one residue showed 42.92 per cent. cupric oxide. The analysis of another showed 50.61 per cent. cupric oxide. This would be in harmony with the assumption of an increasing amount of basic acetate in the residues as the arsenic goes into solution.

We do not wish to lay any great stress on the probable nature of the products of the hydrolysis. We do, however, assert that

all samples of Paris green that we have examined (some of them nearly pure so far as can be determined by all known tests) are decomposed into soluble arsenic; that we have extracted 36.79 per cent. (considerably over one-half) of arsenious oxide from a sample which we have every reason to believe was practically pure, and that in all cases examined the per cent. of copper in the residue increases as the arsenic passes into solution.

It is, of course, reasonable to suppose that the same kind of action takes place with the unground sample, only much more slowly. The Curve "A" shows plainly that the condition of equilibrium has not yet been reached and probably the arsenious oxide would go into solution till the maximum quantity of about 36 per cent. had been reached.

From these experiments it would seem that, while a fair approximation to correct results may be obtained in some cases by suspending Paris green in 1000 parts of water and allowing to stand for a week, the method is quite arbitrary. In none of our work have we noticed any marked change in the rate of solubility at any particular time. On the contrary, the amount of arsenic trioxide in solution appears to depend almost entirely on the length of time of action, the concentration of the solution, and the state of division of the particles of Paris green. To obviate the above difficulties as far as possible, we have used a strong solution of sodium acetate instead of water. The use of such a solution has two advantages. In the first place, arsenic trioxide is much more readily soluble in a solution of sodium acetate than in water, hence much less time is required and consequently there is much less liability to decompose the Paris green.

Of much more importance, however, is the fact that the presence of sodium acetate in the solution largely prevents the hydrolyzing action of water on the compound, thus giving a somewhat sharper distinction between free arsenic trioxide and arsenic trioxide rendered free by hydrolytic action. While we believe this method better than the one in common use, it still leaves much to be desired.

For the determination we digest over the open flame 1 gram of the Paris green for about five minutes with 25 cc. of a solution of sodium acetate containing 12.5 grams of the crystallized salt.

The solution is then cooled, made up to 100 cc. and 50 cc. filtered off and titrated with standard iodine in the usual way.

In connection with this series of experiments, we tried the action of carbon dioxide on Paris green suspended in water. One gram of Paris green from the same sample as was used in the previous experiments and in its original condition, *i. e.*, not pulverized, was suspended in 500 cc. of water for one week, the water being kept saturated with pure carbon dioxide. At the end of this time the arsenic trioxide in solution amounted to 27 per cent. of the weight of the Paris green taken, or 48.5 per cent. of the total arsenic trioxide present had dissolved. There was also a little copper in solution, but this was not determined. The color of the residue changed from a bright green to a dull earthy color, some particles becoming nearly black. Had the sample been pulverized, the decomposition would probably have been practically complete.

As the result of our work, it seems to us that too much importance is being attached to the content of "soluble arsenic oxide" in Paris green. In the first place, since Paris green is of no very definite composition, and since water so easily hydrolyzes it into its constituents, the analytical results for "soluble arsenic" are uncertain and quite dependent on the conditions of the determination. In the usual method of analysis there is no method of distinguishing between the amount of "free arsenic trioxide" and "arsenic trioxide rendered free by hydrolysis." The extent of the hydrolysis is determined mainly by the length of time the water is in contact with the Paris green, and the state of division of the particles. This latter factor exerts by far the greater influence and is wholly beyond the control of the analyst. While the size of the spherical granules is fairly constant in any one sample, different samples show the widest variation. Aside from this variation in the particles themselves, nearly all samples contain a considerable proportion of broken granules of varying degrees of fineness.

Hilgard and others give 4 per cent. as the maximum amount of soluble arsenic trioxide a Paris green should contain if it is to be used for spraying purposes. The purest sample we have obtained gave 2.61 per cent. after standing in water for one week and 4 per cent. at the end of two weeks. A portion from the

sample after being ground was treated in the same way, giving 10.55 per cent. in one week and 17.51 per cent. at the end of two weeks, thus showing both the limitations of the present method of analysis and the marked influence of the state of division on the results.

In view of the fact that carbon dioxide, in the presence of water, so readily decomposes Paris green converting at least one-half of the arsenic trioxide into the soluble condition, it would seem that even if an absolutely pure sample were used in spraying, it might easily happen that the carbon dioxide and water-vapor of the air would convert much more than the limiting 4 per cent. arsenic trioxide into the free state. Probably many of the irregularities observed in the action of Paris green on foliage could be directly traced to weather conditions which happen to be favorable to the formation of free arsenic trioxide from a comparatively pure sample of Paris green.

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NEW BOOKS.

GRUNDZÜGE DER SIDEROLOGIE. VON HANNS FREIHERR V. JÜPTNER.
ERSTER TEIL; DIE KONSTITUTION DER EISENLEGIERUNGEN UND
SCHLACKEN. Leipzig: Verlag von Arthur Felix. 1900. Price, 13 M.

The author of this interesting and valuable work contends that the science of iron, while still far from mature, as we all know, has now become old enough to have a name of its own, and he proposes to call it "Siderology." This name is to be applied to that science which concerns itself not only with the intimate morphological and chemical constitution of iron alloys, but also seeks to determine in what ways these alloys or compounds are affected by outward influences, such as mechanical and heat treatment, and what connection exists between them and the physical and mechanical properties of iron and steel. In the author's view, metallography (Osmond) or siderography (Jüptner) bears the same relation to the science of siderology as petrography bears to the science of geology.

The work is to appear in three parts, of which the present volume of 315 pages is Part First. It covers theory of solution, micrography, the chemical constitution of iron alloys, and the chemical constitution of slags. The second part will treat of the