Each ingot was of the same structure throughout, the caps of pure iron having the same appearance under the microscope as the rest of the ingot. Dark areas, probably of phosphide eutectic, were distributed quite uniformly throughout the ingots. The calcium in this experiment was probably oxidized partially, and perhaps wholly, by oxide of iron.

In the same way calcium was melted with iron containing phosphorus and sulphur. Eight grams of calcium removed all of the 0.37 gram of sulphur present in one ingot, and 11 grams of calcium removed 0.61 gram out of a total of 6.04 grams of phosphorus present in the other ingot, thus reducing the percentage of the latter element from 1.96 to 1.56.

These experiments show:

1. That iron and calcium do not form alloys.
2. That by the reduction of the oxides of carbon the latter element may be introduced into fused metals to which calcium is added.
3. That any commercial application of calcium to the removal or phosphorus from iron is impracticable.

The above observations were made incidental to an investigation of iron alloys, now in progress under a grant from the Carnegie Institution.

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THE CONSTITUTION OF PARIS GREEN AND ITS HOMOLOGUES.

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Received June 28, 1906.

INTRODUCTION.

COPPER aceto-arsenite, under the names of Paris green, Schweinfurt green, and many others, has been a commercial product for nearly a century. The first contribution to its chemistry that I am able to find was made by Liebig.[1] The first definite statement in regard to its composition was made by Ehrmann,[2] working in Liebig's laboratory, who found it to consist of 3 molecules of copper meta-arsenite crystallized with 1

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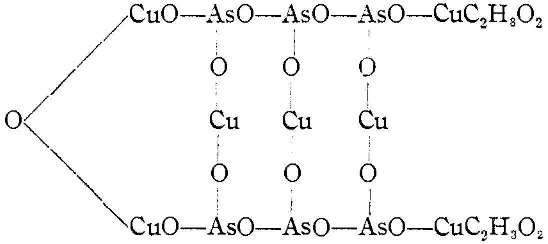
[1] Liebig u. Poggendorf's Handwörterbuch der reinen und angewandten Chemie, 1848, 703.

[2] Ann. 12, 92.

molecule of copper acetate. Abraham[1] found that formic, butyric or valeric acid could be substituted for acetic acid, but does not seem to have made an analysis of the products. Wöhler[2] found that in a butyric green made by him 2 molecules of copper meta-arsenite are united with one of the copper butyrate.

Speculation in regard to the constitution of Paris green have not been wanting, thus Schiff and Sestini[3] suggest the following:



Such a formula would yield

	Per cent.
As_2O_3	47.40
CuO	44.46
$C_4H_6O_3$	8.14

whereas the formula of Ehrmann requires

	Per cent.
As_2O_3	58.55
CuO	31.39
$C_4H_6O_3$	10.06

and numerous analyses of the purest samples do not show a variation of more than 3 per cent. of arsenious acid, 1 per cent. copper and 0.4 per cent. of acetic anhydride from Ehrmann's formula.

In comparatively recent years doubt has been expressed as to whether Paris green of a definite chemical composition can be produced. Six years ago the writer and Beans,[4] as the result of numerous analyses and relying to some extent on the opinions of other chemists, used the expression "Since Paris green is a compound of no very definite composition," etc. Stillman,[5] referring to Ehrmann's formula, says: "This formula is empirical, since a portion of the arsenic may exist as arsenic acid, and copper sub-

[1] Chem. News, 21, 265.

[2] Ann. 94, 44.

[3] Ann. 228, 91.

[4] This Journal, 23, 116.

[5] Chem. News, 80, 250.

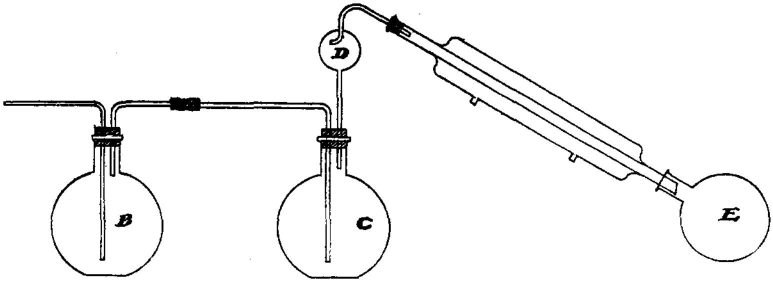
oxide may be present in small amounts with copper oxide." Later work on the part of the writer has convinced him that, while in a measure true, both of the above statements give an erroneous impression. In particular, I have never been able to detect more than minute traces of arsenic acid or cuprous oxide in any carefully prepared samples. However, the variation from Ehrmann's formula in the case of some samples is too great to be explained on the assumption of impurities present in the samples. The present paper presents an attempt to explain these variations and to throw light on the constitution of these important compounds.

EXPERIMENTAL PART.

The analytical methods employed were as follows: The sample in which arsenic was to be determined was dissolved in the smallest possible amount of very dilute sulphuric acid, heating on the water-bath, if necessary. The resulting solution was titrated with standard iodine solution according to the method of the writer and Beans.[1] The presence of a tartrate as given in this method permits of the titration of arsenites containing zinc, nickel, or cobalt in solution as well as copper.

The copper determinations were made by electrolysis of samples from which the arsenic had practically all been volatilized by evaporating nearly to dryness on the water-bath with the addition of strong hydrochloric acid. The copper chloride was then converted into the nitrate by repeated evaporations with small quantities of nitric acid.

The volatile organic acids were determined by decomposing the green in a flask containing an acid potassium sulphate solution. The apparatus is as the following figure shows.



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[1] This Journal, 23, 485.

In B is placed an excess of potassium bisulphate. Steam free from carbon dioxide is passed into the apparatus till the distillate is neutral to phenolphthalein. The steam is then turned off, the sample inserted in B and the distillation continued till the distillate is neutral. Burners under B and C keep the condensation from accumulating in excessive quantity in the flasks. The flask C serves as a trap to retain traces of bisulphate, copper and arsenic. The distillate caught in E was titrated in the usual manner. Several determinations with zinc acetate gave results in accordance with the theory to the second decimal in percentages. The distillate from samples containing arsenious acid showed, in some cases, a faint trace of arsenic which, however, showed practically no acid reaction with phenolphthalein.

The greatest difficulty encountered in the work, and the only cause of uncertainty in the mind of the writer as to the accuracy of the conclusions, is the difficulty in distinguishing between mixtures and true compounds and in preparing the latter, since this class of bodies does not admit of purification by recrystallization. The microscope gives the most satisfactory evidence of the presence or absence of impurities. Free white arsenic and Scheele's green could be readily detected, even when present in minute quantities. The microscopic examination of Paris green is given very fully and clearly by Sattler.[1]

Samples of the green were made in nearly every possible way and several hundred were analyzed. Only such methods of preparation and such analytical data as seem to have a definite bearing on the problem at hand will be given in this paper.

Formic Green.—Formic acid was treated with freshly precipitated copper hydroxide in excess and filtered. The copper present in solution per cubic centimeter was determined. White arsenic was dissolved in sodium hydroxide by boiling, a drop of phenolphthalein added and dilute formic acid added drop by drop till the color was just discharged. The hot solutions of copper and arsenic were mixed in such proportions that 4 molecules of copper oxide were present for 3 molecules of arsenious oxide. The precipitate of Scheele's green was allowed to stand several days till converted into the characteristic brilliant green precipitate. The composition of this precipitate was as follows:

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[1] Z. angew. Chem. 1, 35–47. (Not Z. anal. Chem. 11, 35, as given in Chem. News, 80, 261, and Stillman's "Engineering Chemistry," p. 422; Chem. Pub. Co., 1900.)

	Calculated for $3CuAs_2O_4.CuC_2H_2O_4$. Per cent.	Found. Per cent.
CuO	32.28	32.56
As_2O_3	60.22	59.78
Formic anhydride	7.50	7.70

Acetic Green.—A sample prepared in the same manner as the formic, using acetic instead of formic acid, showed the following composition:

	Calculated for $3CuAs_2O_4.CuC_4H_6O_4$.	Found. Per cent.
CuO	31.39	31.75
As_2O_3	58.55	57.55
Acetic anhydride	10.06	10.31

A very large number of samples of acetic green, made in many different ways, with excess of copper, excess of acetic acid, excess of arsenic, or with an excess of any two of these, showed the presence of 57.3 to 57.7 per cent. of arsenious oxide. The highest result obtained on any sample that appeared free from uncombined white arsenic when examined under the microscope was 58.19 per cent.

Propionic Green.—I find no mention of this compound in the literature of the subject. In preparing it the method used in making the formic green was followed, except that an aqueous solution of white arsenic was used. The green formed was found to be impure under the microscope. Hence it was digested, first with an aqueous solution of white arsenic, then with a solution of sodium propionate. After this treatment all foreign substances seemed to be removed. The analysis gave:

	Calculated for $3CuAs_2O_4.CuC_6H_{10}O_3$. Per cent.	Found. Per cent.
CuO	30.54	30.37
As_2O_3	56.98	56.66
Propionic anhydride	12.48	12.91

Butyric Green.—This green was made in the same manner as the formic green. The analysis gave:

	Calculated for		Analysis given by Wöhler.[1]	
	$3CuAs_2O_4.CuC_8H_{10}O_4$. Per cent.	$2CuAs_2O_4.CuC_8H_{10}O_4$. Per cent.	Per cent.	Found. Per cent.
CuO	29.74	30.11	30.5	29.55
As_2O_3	55.49	49.93	50.1	54.00
Butyric anhydride	14.77	19.96	19.4	16.33

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[1] Ann. 94, 45.

While fully appreciating the difficulties of obtaining pure substances and the limits of analytical accuracy, these analyses seem to point clearly to the following:

Paris green and its homologues are compounds of copper meta-arsenite and a copper salt of the corresponding acid. The ratio most frequently approaches 3:1 but in some cases approaches 2:1. The crystalline structure within these limits and the color do not vary with the composition. Efforts to obtain compounds approaching the ratio of 4:1 or 1:1 were without result, as will be given later in this paper.

To study the effect of the nature of acids in determining the ratio of the copper arsenite and the copper organic salt, solutions of copper formate, acetate and propionate were so made up that the same quantities of copper were present in equal volumes (2.4683 grams CuO in 132 cc.). Exactly the same amount of sodium arsenite (see method of preparing formic green) was added in each case, and like conditions of temperature were maintained. The arsenic trioxide in each was as follows:

	Calculated for $3CuAs_2O_4\ Cu(acid)_2$. Per cent.	Found. Per cent.	Variation.
Formic	60.22	59.23	—0.99
Acetic	58.55	57.47	—1.08
Propionic	56.98	54.77	—2.21

It will be noted that all the figures for the arsenic are below the theory required for 3 of copper arsenite to 1 of copper organic salt, and that the propionic shows a rapid approach towards the ratio of 2:1 as Wöhler found in the butyric. In the same series of acids the stronger the organic acid the more nearly the ratio approaches 3:1. The rule holds true also in the chloracetic acid series which readily form greens.

	Calculated for As_2O_3. Per cent.	Found. Per cent.	Variation.
Trichloracetic	48.64	47.27	—1.37
Monochloracetic	54.83	52.96	—1.87

Green Containing a Dibasic Acid.—All suggestions for structural formulas for Paris green that I am familiar with assume a more or less complicated chain with copper-linking arsenious complexes, terminating with a copper atom at each end, one of whose bonds is saturated with acetic acid. Since, however, acetic acid may be replaced by succinic, such a configuration becomes improbable, since it involves the conception of a very complicated closed chain. The succinic green was prepared as the formic, and was found to contain 57.20 per cent. of arsenious oxide while the ratio of 3:1 would require 58.60 per cent.

In this connection it may be noted that apparently compounds of the type of Paris green may be formed whenever an acid containing a carboxyl group yields a soluble copper salt and forms no complex ions with copper. I have not succeeded in forming greens under other conditions, though numerous attempts were made.

The Action of Various Solutions on Paris Green.—When Paris green of a composition approximately 3:1 is boiled with a solution of arsenious acid in very large excess, if the green be filtered off and dried, a product of more nearly exactly 3:1 in composition is obtained, but I have never been able to obtain a product having the physical properties of Paris green in which the percentage of arsenic trioxide was as high as 58.55 per cent. as the theory for 3:1 requires. If, however, the boiling be continued the green will suddenly become lighter colored and finally change to a blue-green-white product. By repeated treatment with boiling arsenious acid solution the green is converted into copper meta-arsenite.

	Analysis of sample. Per cent.	Calculated for $CuAs_2O_4$. Per cent.
As_2O_3	71.55	71.33
CuO	28.59	28.67

This copper meta-arsenite was pseudomorphic after Paris green. I find no mention of anhydrous copper meta-arsenite in the literature of the subject. The same substance partially hydrated[1] can be made by treating copper hydroxide with an excess of a solution of arsenious acid, allowing to stand for several days, repeating the process and finally boiling for several hours.

ANALYSIS.

	Per cent.
CuO	28.30
As_2O_3	70.13
H_2O	1.57

The color is identical with the preceding. The substance is a gray crystalline powder. I was unable to combine copper meta-arsenite directly with copper acetate to form Paris green.

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[1] Compare Stavenhagen: J. pr. Chem. [2] 51, 1.

By treating Paris green with a neutral solution of copper acetate a brown amorphous powder, pseudomorphic after Paris green, is formed. It contains a higher percentage of copper and a lower percentage of the other constituents than Paris green and is always hydrated. By boiling Paris green with dilute acetic acid the green is slowly dissolved but no marked change in the composition of the undissolved part is to be detected.

Action of Water on Paris Green.—This action is of great practical interest, since soluble arsenic used as an insecticide burns foliage. Notwithstanding the work of several investigators[1] on the subject, Bulletin 151 of the California Experiment Station, p. 19, contains the following paragraph: "Examination by this Station's Laboratory Method.—This takes into account not only the limits of orchard practice with Paris green, but also reckons with the remarkable (?) properties ascribed to Paris green by some chemists when it is treated with plain distilled water; regardless of the fact that this article—acetarsenite of copper—as manufactured to-day, is instantaneously precipitated from complex solutions containing alkali and often excessive quantities of various acids."

A sample of apparently very pure green (composition nearly in the ratio 3:1) was finely pulverized and heated with five hundred parts of distilled water in a sealed tube. Of the original sample there passed into solution,

	Per cent.
CuO	6.46
As_2O_3	24.32
Acetic anhydride	9.27

A sample of the same was boiled for several hours with repeated changes of ammonia-free, carbonic acid-free distilled water. The undissolved portion was finally dried. It showed the following composition:

	Per cent.
Free CuO, not dissolved by cold dilute H_2SO_4	1.48
Combined CuO	49.35
As_2O_3	25.65
Water of hydration and traces of combined acetic acid not determined	......

These figures seem to point out that "plain distilled water" in sufficient quantity would ultimately resolve Paris green into its component parts.

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[1] Haywood: This Journal, 22, 705; Hilgard: Ibid. 22, 690; Avery and Beans: Ibid. 23, 111.

Attempts to Prepare Compounds Analogous to Paris Green Substituting Other Metals for Copper.—As much light had been thrown on the constitution of Paris green by the substitution of other acids for acetic, I endeavored to make similar compounds, using nickel, cobalt, cadmium and zinc in the place of copper. Only zinc gave definite crystalline products.

A solution of zinc acetate containing a little free acetic acid on the addition of an aqueous solution of arsenious oxide deposits a granular white powder, which, under the microscope, appears exactly like certain forms of Paris green except that the balls are white or colorless. The balls are frequently rougher than Paris green balls and the component parts are more easily seen. The individuals appear often in the form of figures g, g_2, h_1, i_1, i_2 as given by Sattler.[1]

The composition of one sample was as follows:

	Calculated for $ZnAs_2O_4$. Per cent.	Found. Per cent.
ZnO	29.13	29.10
As_2O_3	70.87	70.13
Acetic anhydride	......	0.75

Other samples showed as low a percentage of arsenic as 69.5 per cent., from which a higher percentage of acetic is to be inferred. The products, in my opinion, were zinc meta-arsenite crystallized in isomorphic mixtures with zinc acetate and in which the latter was present in small quantities. Zinc meta-arsenite, of which I find no mention in the literature of the subject, can be readily made by dissolving arsenious acid in sodium hydroxide, adding a drop of phenolphthalein, decolorizing with a little dilute sulphuric acid and adding to a hot solution of zinc sulphate. The crystals are of the form just described.

ANALYSIS OF SAMPLE.

	Per cent.
ZnO	28.95
As_2O_3	70.91

The precipitate was free from sulphates.

When zinc butyrate is substituted for zinc acetate and butyric for acetic acid, the precipitate formed by adding arsenious acid may contain as high as 10 per cent. butyric anhydride. In such cases, however, the precipitate is largely mixed with zinc ortho-

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[1] Z. angew. Chem. 1, 37.

arsenite.[1] This higher percentage of the fatty acid, however, shows that butyric acid has a stronger tendency to replace arsenious acid in the zinc as well as in the copper compounds.

In conclusion, I would express my obligations to F. O. Woodruff for his carefully prepared bibliography which he placed at my disposal and to R. Corr and Fred Upson, of this laboratory, without whose careful work in preparing and analyzing compounds, only a small part of which are given here, this work could not have been brought to completion.

THE UNIVERSITY OF NEBRASKA.

A NEW ANALYSIS OF THE WATER OF OWENS LAKE, CALIFORNIA.

BY C. H. STONE AND F. M. EATON.

Received June 30, 1906.

IN the eastern part of California between the White Mountain and Sierra Nevada Ranges, is a V-shaped depression, known as Owens Valley. Measured from crest to crest of the confining mountains, the valley is 10 to 25 miles wide and 125 miles long. The lowest part of the depression is occupied by a saline body of water called Owens Lake. This was originally described as having an area of about 110 square miles, with an average depth of 9 feet 10 inches. The only forms of life inhabiting the water are infusoria, alkali shrimps and the larvae of the alkali flies. There is no outlet, but the lake is fed by the Owens River and a number of small streams, practically all of which enter the valley from the Sierra side. While in the earlier reports it was stated that the loss by evaporation was very nearly counterbalanced by the inflowing water, evidences are abundant to-day that the size of the lake is decreasing. Mr. W. T. Lee, geologist of the U. S. Geological Survey, says in one of his recent bulletins: "The density of the water has increased to a point where sodium bicarbonate precipitates during the winter months without concentration by evaporation. From 1884 to 1894, the lake surface remained practically stationary; from 1894 to 1904 the surface has lowered 16 feet, decreasing the length of the lake by five miles and the width by about two miles."

Owens Lake is probably the largest natural soda deposit in the world. Thirty years ago, Loew estimated that it contained

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[1] Bloxam: J. Chem. Soc. 15, 296 (1862).