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REPORT OF ANALYSES OF PARIS GREEN AND
OTHER INSECTICIDES IN 1900.

L. L. VAN SLYKE AND W. H. ANDREWS.



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REPORT OF ANALYSES OF PARIS GREEN
AND OTHER INSECTICIDES IN 1900.*

L. L. VANSLYKE AND W. H. ANDREWS.

SUMMARY.

In accordance with the provisions of a law designed to protect purchasers of Paris green, samples were secured during 1900 and the results are published in this bulletin.

Paris green contains as its chief constituent a compound called copper aceto-arsenite, which, when chemically pure contains :

Arsenious oxide	58.64	per ct.
Copper oxide,	31.30	“
Acetic acid,	10.06	“

In the 22 samples of Paris green examined, the arsenious oxide varied from 55.83 to 60.80 per ct. and averaged 57.05 per ct. The water-soluble arsenious oxide varied from 0.61 to 15.69 per ct. and averaged 1.68 per ct.

The copper oxide varied from 27.22 to 31.20 per ct. and averaged 30.02 per ct. The amount of arsenious oxide for each pound of copper oxide varied from 1.81 to 2.24 and averaged 1.89 pounds. The impurity most commonly found was white arsenic and this did not appear to be excessive. The general result of the examination is to show a good quality of Paris green in the market at the time the samples were taken.

There are given in addition, analyses of Arsenoid, Paragrene, Black Death, Bug Death, and Hammond's Slug Shot.

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INTRODUCTION.

During the year 1900, there were collected for analysis twenty-two samples of materials sold as Paris green, and also one sample each of Arsenoid, Paragrene, Black Death, Bug Death and Hammond's Slug-Shot. Of the twenty-two samples of Paris green analyzed, ten represent firms whose goods were not examined by us in 1899.

CHEMICAL COMPOSITION OF PARIS GREEN.

Paris green, or copper aceto-arsenite, may be regarded, when chemically pure, as containing approximately

Copper arsenite	82 per. ct.
Copper acetate	18 "

However, it is customary, when speaking of the amount of arsenic contained in Paris green, to refer to it as arsenious oxide, and similarly the amount of copper is referred to as copper oxide. Arsenious oxide, as such, and copper oxide, as such, are not present in pure Paris green, and the use of these terms in giving the results of chemical analysis is simply a convenient custom. Using the usual form of expression, as thus explained, we should give the composition of pure copper aceto-arsenite as follows:

Arsenious oxide	58.64 per ct.
Copper oxide.....	31.30 "
Acetic acid	10.06 "

When we say that this compound in pure form contains 58.64 per ct. of arsenious oxide, we mean that the amount of arsenic present simply is equivalent to the quantity of arsenious oxide stated, and not that arsenious oxide is present to that or any other extent in the compound known as copper aceto-arsenite.

Now, Paris green, as found in the market, rarely, if ever, consists entirely of pure copper aceto-arsenite, but contains this compound as its chief constituent, with varying proportions of other substances. The varying composition of Paris green is usually due to variations in care given to the details of the process of manufacture.

Methods of chemical analysis.—The total arsenic was determined by the method proposed by Thorn Smith (*Jour. Am. Chem. Soc.*, **21**: 769) as modified by J. K. Haywood (same journal, **22**: 576.) In determining the water-soluble arsenic, J. K. Haywood's method was used (*Jour. Am. Chem. Soc.*, **22**: 578), except that the Paris green was treated twenty-four hours for extraction at the rate of one part by weight of Paris green to 1,000 parts of distilled water. The copper was determined by electrolysis.

ANALYSES OF SAMPLES OF PARIS GREEN.

Sam- ple num- ber.	Name of manufacturer.	Total arseni- ous oxide.	Water- soluble arseni- ous oxide.	Copper oxide.	Crystals of arseni- ous oxide present as shown by micro- scopic examina- tion.	Solubility in strong ammonia.	Retail price per pound.
		<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>			<i>Cents.</i>
105	Acme Color Works.....	56.56	1.35	30.20	Very few.....	Complete.....	25
43	Acme Color Works.....	56.50	1.10	29.89	Few.....	Complete.....	25
52	Adler Color and Chemical Works.....	56.25	1.59	29.85	Few.....	Nearly complete in 24 hours.....	25
101	Adler Color and Chemical Works.....	56.75	1.23	30.54	Few.....	Nearly complete in 24 hours.....	20
40	A. B. Ansbacher & Co.....	56.81	0.61	30.33	Very few.....	Complete.....	25
104	A. B. Ansbacher & Co.....	56.75	1.10	29.98	Few.....	Complete.....	30
50	James A. Blanchard.....	59.20	15.99	6.86	Much foreign matter.....	Slightly.....	30
41	James A. Blanchard.....	58.16	0.74	28.53	None.....	Incomplete in 24 hours.....	25
45	Cawley, Clark & Co.....	56.62	0.74	31.20	Numerous.....	Complete.....	40
35	Chas. M. Childs & Co.....	57.17	0.74	30.33	Few.....	Complete in 24 hours.....	18
49	Eckstein Bros.....	57.11	1.10	28.76	Few.....	Complete in 24 hours.....	25
51	M. Herrmann & Co.....	56.62	1.23	30.16	Few.....	Complete.....	25
47	Highlands Chemical Co.....	57.11	0.98	30.39	Few.....	Complete.....	30
37	Fred L. Lavanburg.....	56.50	0.86	30.16	Few.....	Complete.....	20
48	Leggett & Bros.....	56.93	1.10	30.39	Few.....	Complete in 24 hours.....	25
42	N. Y. Enamel Paint Co.....	56.75	1.59	29.45	Very few.....	Complete.....	25
36	John C. Lucas.....	55.83	0.98	30.73	None.....	Complete.....	25
34	L. Pfeiffer.....	56.75	0.74	30.16	Very few.....	Complete.....	22
33	C. T. Reynolds & Co.....	60.80	0.98	27.22	Few.....	Complete.....	22
102	C. T. Reynolds & Co.....	57.05	0.86	30.70	Few.....	Complete.....	20
103	C. T. Reynolds & Co.....	56.75	0.86	30.39	Numerous.....	Complete.....	20
44	Not given.....	56.17	0.86	30.23	None.....	Complete.....	25

DISCUSSION OF RESULTS OF CHEMICAL ANALYSIS.

1. *Total arsenious oxide.*—In the 22 samples of materials sold as Paris green, examined by us, the amount of arsenic, equivalent to arsenious oxide, varies from 55.83 to 60.80 per ct., and averages 57.05 per ct. This average is about one-half of one per ct. higher than that found last year, and is about one and one-half per ct. below the equivalent of arsenious oxide contained in pure copper aceto-arsenite. So far as the total arsenic content is concerned, the amount found indicates a high quality of Paris green. The variation is about the same as last year and, excepting two samples, is within surprisingly narrow limits. The lowest amount of arsenious oxide is nearly six per ct. above that required by law, viz.: 50 per ct. Were the total amount of arsenic present in Paris green the only point to be considered, the quality would be regarded as very satisfactory, but we must consider at the same time the amount of water-soluble compounds of arsenic present in Paris green.

2. *Water-soluble compounds of arsenic.*—The presence of water-soluble arsenic in Paris green is seriously objectionable, owing to the fact that soluble arsenic compounds injure foliage. Hilgard, of California, states that in the dry climate of California Paris green injures foliage, when it contains an equivalent of more than four per ct. of arsenious oxide in the form of water-soluble arsenic compounds. The water-soluble arsenic most commonly occurring in Paris green is in the form of arsenious oxide, commercially known as common white arsenic.

The method of analysis used by us in determining the amount of water-soluble arsenic compounds in Paris green should show the full amount of such compounds that would be found in actual field work where Paris green is mixed with water at the rate of one part by weight of Paris green to 1000 parts of water and the mixture used soon after preparation. By longer extraction with water, larger quantities of soluble arsenic compounds can be obtained; but for our purpose, it is desirable to approximate the amount likely to be found in actual field practice in the use of Paris green under the conditions commonly employed. It would, in our judgment, be proper to condemn for use as an insecticide

Paris green or other similar materials that yield more than four per ct. of water-soluble arsenic compounds expressed as arsenious oxide, when treated for 24 hours with distilled water at the rate of 1000 parts of water for one part of Paris green or arsenic-containing materials.

The water-soluble arsenious oxide varies in the 22 samples of Paris green examined from 0.51 to 15.69 per ct. and averages 1.68 per ct. Excluding sample No. 50 from the average, the amount of water-soluble arsenious oxide in the remaining 21 samples is a trifle over one per ct., very far below limit of harm prescribed for use as an insecticide. Sample No. 50 is to be condemned as wholly unfit for insecticidal purposes on account of the very large excess of arsenic compounds present in water-soluble forms.

3. *Copper in Paris green determined as copper oxide.*—The amount of copper expressed as the equivalent of copper oxide, varies in the 22 samples of Paris green examined from 6.86 to 30.73 per ct., and averages 28.97 per ct. However, sample No. 50 is clearly shown by its low copper content not to be Paris green at all or, at least, to contain only a small proportion of Paris green and we may properly exclude this from our average. Then in the remaining cases the average is 30.02 per ct. of copper oxide, about the same as last year.

4. *Relation of copper oxide to arsenious oxide in Paris green.*—In pure copper aceto-arsenite there are 1.87 pounds of arsenious oxide for one pound of copper oxide. Now, this relation is of value in showing whether Paris green contains more arsenious oxide than it ought. The chief adulterant used in Paris green is arsenious oxide, commercially known as white arsenic. This is used because it is cheaper than Paris green and also because it can be safely added without any danger of reducing the amount of arsenious oxide. In fact, a very poor quality of Paris green can be brought up to the legal requirements by addition of arsenious oxide. However, arsenious oxide cannot be added to Paris green without increasing the ratio of arsenious oxide to copper oxide above 1.87. In the samples examined, excluding No. 50, the ratio of arsenious oxide to copper oxide varies from 1.81 to 2.24 and averages 1.89. In sample No. 33, the arsenious oxide exceeds 60 per ct. and the copper is less than 28 per ct.;

hence, the arsenious oxide is present in amounts more than twice exceeding the copper oxide. In other words, there is too much arsenious oxide for the copper oxide present and the only possible inference is that white arsenic or some other arsenic compound has either been added purposely or is present as the result of carelessness in manufacture.

5. *Results of microscopic examination.*—In Bulletin No. 126 of the California Experiment Station, the microscopic examination of Paris green for adulteration, especially that of uncombined arsenious oxide (common white arsenic) is highly recommended. This test in our hands has been found helpful as an adjunct, but can not take the place of chemical analysis. We can not in our work see any definite relation between the number of crystals of arsenious oxide shown by the microscope and the amount of water-soluble arsenious oxide as shown by chemical determination. So far as our experience with the samples examined goes, microscopic examination cannot be relied upon to distinguish with certainty a Paris green containing an injurious amount of water-soluble arsenic.

6. *Solubility of Paris green in ammonia.*—The solubility of Paris green in ammonia is a useful test for detecting the presence of insoluble adulterants like barium sulphate, calcium sulphate and similar materials. It cannot, however, be regarded as an entirely reliable test for detecting the presence of arsenious oxide or common white arsenic, the most common impurity of Paris green.

7. *General conclusion as to purity of Paris green in market.*—Our results indicate a satisfactory condition as to the arsenic content of Paris green found in the market during 1900, and the same can be said as to the amount of water soluble compounds present in the samples examined, excepting only No. 50.

EXAMINATION OF MISCELLANEOUS INSECTICIDES.

ANALYSIS OF ARSENOID.

The sample examined was made by the Adler Color and Chemical Works of New York City and contains :

Total arsenic equivalent to arsenious oxide.....	58.82	per ct.
Water-soluble arsenic equivalent to arsenious oxide.....	2.94	" "
Copper equivalent to copper oxide.....	30.76	" "
Moisture.....	1.91	" "

ANALYSIS OF PARAGRENE.

One sample of this material was found to contain :

Total arsenic equivalent to arsenious oxide.....	36.11	per ct.
Water-soluble arsenic equivalent to arsenious oxide....	1.47	" "
Copper equivalent to copper oxide.....	17.87	" "
Calcium equivalent to calcium oxide.....	14.20	" "
Moisture.....	8.15	" "

ANALYSIS OF BLACK DEATH.

Moisture.....	9.78	per ct.
Sulphate of lime (gypsum).....	45.34	" "
Magnesium oxide.....	3.98	" "
Iron and aluminum oxide.....	3.02	" "
Arsenious oxide.....	0.79	" "
Copper oxide.....	0.41	" "
Silica.....	5.42	" "
Loss on ignition.....	28.91	" "

Whatever efficiency this material may have as an insecticide is not due to the Paris green or other arsenic compounds contained in it.

ANALYSIS OF BUG DEATH.

Moisture.....	0.25	per ct.
Zinc oxide.....	86.80	" "
Iron oxide.....	5.20	" "
Lead oxide.....	2.01	" "
Silica.....	2.96	" "
Loss on ignition.....	2.43	" "
Phosphoric acid.....	0.03	" "
Nitrogen.....	0.04	" "
Potash.....	0.00	" "

Some claims are made for this material as a fertilizer, but the claims are not supported by the results of analysis.

HAMMOND'S SLUG SHOT.

Moisture.....	10.88	per ct.
Sulphate of lime (gypsum).....	74.72	" "
Arsenious oxide.....	1.04	" "
Copper oxide.....	0.59	" "
Iron and aluminum oxides.....	3.15	" "
Silica.....	2.77	" "
Loss on ignition.....	6.78	" "

DEFECTS OF PRESENT PARIS GREEN LAW.

In its present form the Paris green law of this State is seriously defective in several respects, most prominent of which are the following :

1st. The present law wholly fails to protect consumers from adulteration of Paris green by water-soluble arsenic compounds, the most common of which is uncombined arsenious oxide or common white arsenic.

2d. The total amount of arsenic required in Paris green by the present law, viz., the equivalent of 50 per ct. of arsenious oxide, is needlessly low. In our examination of Paris green as sold in this State during the past two years, the lowest amount of arsenic found was 55.34 per ct., over five per ct. above the present required standard.

3d. The law fails to require that the arsenious oxide in Paris green should be in combination with copper. This omission offers opportunity for serious abuse. Sample No. 50 offers a good illustration of this. In that case there is not one-fourth as much copper as should be present to combine with the arsenic.

In order to remedy these defects, the section of the law that so completely fails to define Paris green should be changed so as to cover the following points :

1st. Paris green should be required to contain an amount of arsenic in combination with copper equivalent to 54 per ct. of arsenious oxide.

2d. Paris green should be legally declared adulterated if it contains arsenic in water-soluble forms equivalent to more than three per ct. of arsenious oxide.