
Bulletin No. 58, : : August, 1894.


Agricultural Experiment Station

—OF THE—

AGRICULTURAL AND MECHANICAL COLLEGE,
AUBURN, : : ALABAMA.

Paris Green ; Composition and Adulterations.

B. B. ROSS, State Chemist.

 The Bulletins of this Station will be sent free to any citizen of the State on application to the Agricultural Experiment Station, Auburn, Ala. All communications should be addressed to
EXPERIMENT STATION, AUBURN, ALA.

Published by order of the Board of Direction.

BROWN PRINTING CO., STATE PRINTERS, MONTGOMERY, ALA.

BOARD OF VISITORS.

COMMITTEE OF TRUSTEES ON EXPERIMENT STATION.

I. F. CULVER Union Springs.
J. G. GILCHRIST..... Hope Hull.
H. CLAY ARMSTRONG..... Auburn.

BOARD OF DIRECTION.

WM. LEROY BROUN President.
A. J. BONDURANT Agriculturist.
B. B. ROSS..... Chemist.
P. H. MELL..... Botanist and Meteorologist.
J. M. STEDMAN Biologist.
C. A. CARY, D. V. M..... Veterinarian.

ASSISTANTS:

J. T. ANDERSON..... First Assistant Chemist.
R. E. NOBLE..... Second Assistant Chemist.
C. L. HARE..... Third Assistant Chemist.
R. L. BIVINS..... Clerk, and Assistant Botanist.
T U. CULVER..... Superintendent of Farm.

INSECTICIDES.

COMPOSITION AND ADULTERATION.

The employment of insecticides in combating and checking the ravages of the cotton worm, has been generally practiced in the cotton growing sections of the South for many years, and where proper precautions have been observed, with undoubted success.

The materials which are almost exclusively utilized by the cotton planter as insect poisons are Paris Green, and London Purple, though the consumption of the former far exceeds that of the latter.

While these substances have been so generally employed for such a long period of time, but little attention has been paid to the quality and purity of the materials purchased for use as insecticides, and it is not at all surprising that frauds and adulterations are occasionally found upon the market.

With a view to determining whether or not such adulterations or falsifications had been practiced upon goods of this class for sale in this State, an attempt was made to secure samples of Paris Green and London Purple from all sections of the State. A large number of circular letters, calling for samples of these insecticides, were sent out to parties in all portions of the State, and it was expected that quite a number of specimens would be obtained in this way. But few replies, and still fewer samples were received, however, and the investigation has consequently been more limited in scope than was originally intended.

With one exception, the samples came from the "black belt," where the employment of Paris Green, has been much more extensive than on the hill lands; in fact in some of

the hill counties, it has been found impossible to secure Paris Green in the market. Not a single sample of London Purple, could be obtained, a circumstance that indicated that this insecticide was even less in demand than was the case several years since.

Commissioner H. D. Lane, through Maj. T. J. Key, very kindly co-operated in securing additional samples of Paris Green, and these with the samples already on hand enabled the formation of a fair estimate of the character and quality of the insecticides on the market in Alabama.

The substance sold under the name "Paris Green" is, chemically considered, an aceto-arsenite of copper, and is known in the arts and to the trade under quite a variety of names, such as, "Emerald Green," "Mitis Green," "French Green," "Schweinfurt Green," etc.

The last named term (derived from the place of it's first manufacture) is the designation most frequently given to it in Europe, it being there used largely as a pigment on account of it's brightness of color.

Scheele's green, the simple arsenite of copper, is frequently confounded with Paris Green, but it is distinguished from the latter by its duller color and the entire absence of acetic acid, which is a characteristic constituent of a genuine Paris Green.

One of the methods formerly employed in the preparation of Paris or Schweinfurt Green involved the simple treatment of the crude and freshly precipitated Scheele's green (copper arsenite) with wood vinegar, from which source the acetic acid of the final product was derived.

The process as first devised by Russ & Sattler in 1814, was kept secret for a long period, but after the investigation of its composition by Liebig, its manufacture became more extended.

In the method generally adopted for the preparation of this substance, arsenious acid (white arsenic) and acetate of copper (verdigris) are employed; both are dissolved separately in hot water, and the boiling solutions are mixed to-

gether, the precipitated coloring matter being allowed to settle.

Paris Green is normally a bright crystalline powder, insoluble in water, but changing in color when boiled with water for some time. According to Ehrmann, the composition of pure Paris Green is as follows :

| | |
|---------------------|-------|
| Copper oxide..... | 31.29 |
| Arsenious acid..... | 58.65 |
| Acetic acid..... | 10.06 |

The purest grades of Paris Green, however, show at least slight variations from the proportions given above, and it is quite difficult to fix an absolute standard for the composition of products of this character.

Paris Green, which is intended for use as an insecticide, however, should contain at least 50 per cent. of combined arsenious acid, and any purchasers of this article who are in doubt as to its purity or quality can have the same tested by forwarding a sample to this Laboratory.

The following is the result of the examination of the samples of Paris Green received at this Laboratory :

| | Arsenious acid. |
|--|-----------------|
| No. 1. From Hale Co., forwarded by Mr. L. Garber..... | 55.42 |
| No. 2. From Wilcox Co., forwarded by Mr. S. M. Cathcart..... | 55.01 |
| No. 3. From Montgomery, forwarded by Dept. of Agriculture..... | 59.71 |
| No. 4. From Montgomery, forwarded by Dept. of Agriculture..... | 53.13 |
| No. 5. From Montgomery, forwarded by Dept. of Agriculture..... | 57.38 |
| No. 6. From Eimer & Amend, New York.... | 54.15 |
| No. 7. From Tallapoosa county..... | none. |

Samples one to six inclusive, possessed the bright green color characteristic of a genuine Paris Green, and their mechanical condition was all that could be desired.

The proportions of arsenious acid are also well above the limit previously referred to (50%), and no traces of adulteration or attempts at adulteration were detected.

Sample No. 7, although of nearly the same shade of color as a normal Paris Green, was nevertheless so lacking in the brightness of tint which characterizes the genuine article that it was at once regarded with suspicion. A qualitative examination, carefully conducted, showed an entire absence of both copper and arsenic, not the least trace of the latter being discoverable by the employment of the most delicate tests. Quite a number of tests were next made for all the green coloring agents of importance, but with negative results, and it was then decided that the color of the material was due to a combination of blue and yellow coloring matters.

A further examination revealed the presence of Prussian Blue and chrome yellow, intimately mixed with each other, and well incorporated with a large quantity of inert materials, such as clay, chalk, etc.

On taking a small portion each of Prussian Blue and Chrome Yellow and mixing with a large quantity of clay or chalk, it was found that a product corresponding almost precisely in color to the material examined, could be produced, and it was found quite easy to imitate the normal shade of color of Paris Green, though, as before stated, the brightness of tint, would be lacking. It was estimated that a material of this character could be manufactured at a cost not exceeding one cent per pound, while a high grade Paris Green frequently costs above twenty cents per pound, the fraudulent manufacturer being thus able to dispose of his product at an enormous profit.

Of course, such a preparation as this is entirely worthless as an insecticide, and planters using such an article, and not being aware of its character, would probably be thereafter prejudiced against the use of insect poisons in any shape or form.

As before stated, the true character and quality of an insecticide can be readily ascertained by analysis, and the

Station Laboratory will cheerfully test any samples forwarded for examination by planters from any section of the State.

Any fraudulent goods of this character can thus be readily driven from the market, and the planter can then be assured as to the absolute purity of the insecticides which he may purchase.

METHOD OF ANALYSIS.

The following is the process adopted in the Laboratory for the determination of arsenious acid in Paris Green :

Weigh one gram of the material, and place in a medium size beaker or flask ; add about 30 cubic centimetres of strong hydrochloric acid and digest on a water bath, at a temperature somewhat below the boiling point, adding at frequent intervals, small quantities of finely powdered potassium chlorate. Continue the heating until the odor of free chlorine has almost disappeared ; dilute with water, and filter, if necessary. Add ammonia in slight excess, cool and add magnesia mixture gradually, stirring vigorously all the while. Allow to stand 12 hours, filter and wash precipitate with ammonia water.

Dry filter and contents : detach precipitate from filter as completely as possible ; ignite filter, using ammonium nitrate solution to facilitate ignition. Transfer the precipitate to a porcelain crucible, and heat for a while on an iron plate, and finally with the direct flame. Add filter ash to the precipitate and weigh as magnesium pyro-arsenate.

(NOTE.—Of course, this method is only applicable in the absence of phosphates and arsenates.)

