Lactic Green*

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Paris green has been known as a pigment since the 18th century, but it was 1868 before its use as an insecticide became popular. It was first used in the fight against the Colorado potato beetle (2), and has since been used as both powder and spray in combatting the spread of various insects. "Its chief disadvantage lies in the fact that it contains soluble arsenic and is very apt to burn the foliage. . . . For this reason, and because it is harder to keep in suspension in water and does not adhere permanently to foliage, it has been supplanted by arsenate of lead for many purposes" (2). Dearborn in a patent (3) and a series of papers (4-8) describes numerous homologs of acetic green. Of those that were tested a few were found to be slightly more toxic than Paris green, but they became too insoluble as the length of the fatty acid chain increased.

Since lactic acid contains an hydroxyl group in addition to the carboxyl group, a green prepared from it should, in part, overcome the objection of insolubility, and adhere better to the foliage. In a patent, Balint (1) states that copper lactate, as well as other aliphatic acid radicals can replace copper acetate in the preparation of Paris green. He, however, does not describe the lactic green, and no additional references to it have been found. Following the suggestion of Dearborn (8) that light density products should be given preference over the heavy ones often found on the market, both Paris and lactic greens were prepared according to the method of Webster (9). The Paris green prepared by this method was blue-green, and the lactic-green an olive-green.

As a result of testing numerous suggested methods under varying conditions, the following were found necessary if a desirable product is to be obtained.

1. The concentration of the ingredients should be kept as high as possible. Attempts to prepare the greens from dilute solutions lead to poor yields.

2. The pH of the reaction mixture must be controlled. If excessive amounts of the acid or alkali are used, the greens will dissolve. This is especially true in the case of the lactic green, and in the preparation of this compound, time must be allowed for the anhydrides to hydrolyze.

3. The copper sulfate and other reagents should be free of iron, as the iron causes brown spots in the filter cake.

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4. The directions given in Webster's patent (9) lead to the formation of desirable products, provided the copper sulfate is free of iron.

In accordance with the above suggestions, Paris and lactic greens were prepared. Two solutions were used in each case:

1. 216.5 g. $CuSO_4 . 5H_2O$ + 275 ml. water, and
2. 129 g. As_2O_3 + 85 g. Na_2CO_3 + 300 ml. water.

Solution 2 was heated to boiling and added to solution 1 at 60-70°. After the reaction had subsided, 25 ml. of glacial acetic acid or 39 ml. of 85% lactic acid was added. The mixtures were heated on a hotplate for 30 minutes, and then filtered and washed. The filtrate from the lactic green contained more copper than that from the Paris green. The residues were dried on a hot plate over night. Yield: Paris green, 209.5 g.; lactic green, 210.3 g. Theoretical: 222 g. and 233 g., respectively.

The two greens were tested, by J. J. Davis and G. E. Gould, Department of Entomology, Purdue, both in the greenhouse and on the field, and found to be equal in their insecticide properties. They were equally destructive to the foliage of sensitive plants such as the bean, and adhered to the foliage equally well. In one case the plants were sprayed with the two poisons at a dilution of one pound in 50 gallons of water, to which two pounds of hydrated lime had been added. The following day two plants of each plot were potted and covered with cages. Thirty Colorado potato beetle larvae, of various sizes, were introduced onto each plant, and the counts of the dead and live insects were made 4 days later. On the Paris green sprayed plants 28 and 27 dead larvae were found, and on the lactic green sprayed plants 27 and 25 dead larvae.

Summary

Lactic green can be prepared by the same methods used in the preparation of Paris green. It has been found that the greens are best prepared by the method of Webster and that they are equal in respect to adherence to foliage, burning of foliage, and insecticide properties.

Bibliography

1. S. Balint, Brit. Pat. 483,739, Apr. 26, 1938.
2. J. J. Davis, Bull. of Purdue University **32**, No. 7, 15 (1932).
3. F. E. Dearborn (for free use), U. S. Pat. 2,104,584, Jan. 4, 1938.
4. Ibid., J. Econ. Entomol., **28**:710-14 (1935).
5. Ibid., **29**:445-9 (1936).
6. Ibid., **30**:140-3 (1937).
7. Ibid., **30**:804 (1937).
8. Ibid., **30**:958-62 (1937).
9. B. P. Webster (to Chipman Chem. Co., Inc.), U. S. Pat. 1,928,771, Oct. 3, 1933.