FREE ARSENIOUS OXIDE IN PARIS GREEN.

BY E. W. HILGARD.

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IN view of the many reclamations and conflicting results as to the content of free arsenious oxide in commercial Paris green that have reached this station since the publication of Bulletin No. 126, in which the unsatisfactory quality of the average material now on the market was discussed, it seems desirable to review briefly some of the causes of the discrepant results of different analysts.

The serious injury to foliage frequently resulting from the use of the commercial article led this Station to investigate specially the subject of the presence and correct determination of free As_2O_3. It should be understood that in the arid climates, where practically no rain falls during the summer, the absence of the periodic washing-off of the leaves, such as frequently recurs in the region of summer rains, permits of injury from a much smaller percentage of the free arsenical compound. The limit above which such injury occurs was found by our experience to be 4 per cent. of free arsenious oxide ; and whenever that amount is exceeded we recommend the addition of a certain proportion of slaked lime to counteract its effects.

The New York law requiring the total percentage of arsenious oxide in Paris green to be "not below 50 per cent.," wholly omits any reference to the free or combined state of the compound. Hence some manufacturers have discarded all care in this respect, and greens containing as much as 20 per cent. and more, of the free oxide, are of frequent occurrence. Such articles are extremely objectionable in this climate at least, and probably elsewhere. This law certainly needs amendment, as it puts a premium on careless manufacture, or fraud. In some samples submitted to us it was evident that the "white arsenic" had been added in bulk to the green, as in the case of other adulterants, among which gypsum, Glauber's salt, chalk, and pipe-clay were easily identified by the microscope as well as by chemical tests. Microscopic examination proved, in fact, to be such a convenient and decisive test in most cases, that it is always the first thing we do, as it frequently renders any further chemical work wholly unnecessary. The cogency of the microscopic examination is not so generally appreciated by chemists as it is by mineralogists ; but there is no excuse for any mistakes in such work, as the crystalline forms of adulterants are perfectly conclusive, either directly, or after solution and evaporation. Especially can there be no mistake about the lustrous, sharp octahedrons of arsenious oxide, whether they be scattered about among the globules of Paris green, or, as is most commonly the case, adherent to the surface of the latter ; so that in case of large proportions of the free arsenic, the globules are set with sharp octahedrons like a circular stone-saw or "diamond-drill." In most of such samples we have found the bulk of the free arsenic to be in this condition.

Such crystals dissolve very slowly in cold water, and even when 40° or 50° C. is used ; and as a high temperature disintegrates the green globules, it does not seem admissible to employ it. After twenty-four hours' treatment with indefinite quantities of cold water, the arsenical crystals were sometimes still discernible as transparent, obtuse ridges around the outside of the globules, still constituting quite one-half of the total free arsenious oxide.

It is thus obvious that by treatment of Paris green for a few hours, with such small amounts of water as we find are in use at some of the Eastern stations (100 to 300 cc. per gram of green), too low results must be obtained. As in orchard practice the proportion of water used is from 500 to 1000 times the weight of the green employed, it seems proper to conform the analytical practice to this practice, in order to obtain results that shall represent the actual facts of the case. This is what we have adopted as a rule, together with the prolonged agitation of the green with the water, which is likewise practiced in the orchard. It is from this cause, doubtless, that our results are almost uniformly above those of our Eastern colleagues ; but I think we are justified in adhering to what is manifestly in accordance with the practical outcome. It has been repeatedly said to us, in reply to our insistence on the microscopic examination, that "no Eastern chemist practices it." To this I have only to say, that in this as in numerous other cases, the microscopic examination usually affords so much more prompt and decisive information regarding purity or adulteration than mere analysis, that I cannot but regard its omission as a serious mistake, in neglecting important evidence so readily obtainable.

It has been suggested that we do not take into account the "solubility of Paris green in water," as estimated from the amount of copper going into solution. But as in several cases we have found verdigris to pass into the first filtrates, the dissolution of copper being reduced to a mere trace when the washing was continued beyond 1000 cc. per gram, it is manifest that this correction cannot be applied safely without special precautions, even if it were certain that Paris green is soluble; in any case, the arsenic that passes into solution in this form cannot exceed a fraction of 1 per cent. In the case of a sample containing somewhat less than 4 per cent. of free arsenious oxide, for which an Eastern chemist has reported only 0.9 per cent., we found in the first 1200 cc. applied to 1 gram of substance, 0.26 per cent. of copper, for which, supposing it to represent Paris green. a similar weight of arsenious oxide would have to be deducted. But an additional 600 cc. failed to give *any* reaction for copper, even when concentrated to 25 cc., although a small amount of arsenic still continued to come. The microscope showed the cause of this continued slight contamination to be a few readily recognizable octahedrons of arsenious oxide adherent to the surface of the globules, here and there. Practically the same results were obtained by a slow percolation of cold water, when after the passage of 2000 cc. no copper reaction could be found; but a trace of arsenic continued to come through at the end of the fifth liter of water. In the sample thus washed, however, no arsenical crystals could be detected by the microscope, but only fragments of crushed globules of Paris green, whose form and aspect cannot be mistaken for arsenious oxide by any practiced eye.

It is thus obvious that extraction with a few hundred cc. of water for a few hours cannot yield a proper measure of the free arsenic present in Paris green. Not less than 600 cc., and preferably not less than 1000 cc., or 1 liter per gram, should be employed, and the extraction continued for twenty-four hours.

As to the test prescribed by at least one Eastern station, *viz.*, the solubility of the pure green in ammonia, it is utterly illusory so far as "white arsenic" is concerned. Even if the latter were not itself rather readily soluble in ammonia, the fact stated in all books of reference that it is easily soluble in ammonium arsenite (which is of course formed when Paris green is dissolved in ammonia) fully disposes of any claim of this test to acceptance.

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A METHOD OF DETERMINING FREE ALKALI IN SOAPS.

BY R. E. DIVINE.

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THE usual method of making this determination prescribes a separation of caustic from carbonated alkali by drying the soap, dissolving in absolute alcohol, and after filtering and washing the undissolved carbonate with alcohol and dissolving in water to titrate the solutions containing caustic and carbonate, respectively, with standard acid. This method is open to several objections, aside from the amount of time consumed. If it is desired to obtain accurate results on the caustic and carbonate separately, the preliminary drying of the soap introduces an error since the caustic alkali will take up carbon dioxide from the air unless the drying is done out of contact with air. It is quite a troublesome process to filter an alcoholic soap solution if one is not provided with appliances to keep the funnel hot during filtration. Dudley and Pease[1] use an alcoholic solution of stearic acid for titrating the caustic, but still filter from undissolved carbonate, and determine the latter in the usual manner. In the following process the writer has succeeded in eliminating filtration. For this method it is necessary to provide three standard solutions:

1. Hydrochloric acid, N/10 (for standardizing 2).
2. Caustic soda, N/10, in alcohol.
3. Stearic acid, N/10, in alcohol.

2 and 3 should be exactly equivalent one to the other, titrated warm with phenolphthalein indicator.

Two grams soap (which needs no drying) is weighed into a round-bottomed flask, of about 300 cc. capacity, and 50 cc. alcohol poured upon it. N/10 stearic acid is now run in from a

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[1] *Engineering and Railroad Journal*, (1891), 551.