

or increase the arsenic oxide by some means. To obviate this difficulty, therefore, a maximum per cent of total arsenic oxide in hydrogen or acid arsenate should be specified and another amount for the neutral or basic arsenate.

A comparison of the amounts of water-soluble arsenic obtained by each method shows that the greater percentage is always found by the Oregon Station method. From these figures it is obvious that all the water-soluble arsenic oxide is not obtained by the official method; nor are the results obtained by the Oregon Station method too high, due to possible hydrolysis or other chemical action upon the sample, for in the three cases, Samples 3, 4 and 6, where only a trace is reported present by the official method, identical results are obtained by the Oregon Station method. These latter results further substantiate the claim made in our previous paper that the pure arsenates of lead are extremely insoluble, and when there is any free-arsenic oxide found it is due to the arsenic being in the form of a soluble salt and not in the form of either the hydrogen or basic arsenate. It should also be noted that no soluble lead oxide was found by either method, which is further proof that the water-soluble arsenic oxide was not in the form of a soluble lead salt.

As additional proof that all the water-soluble arsenic oxide is not obtained by the official method, a glance at the two columns depicting the quantity of water-soluble solids or impurities found shows that the greater amount is consistently obtained by the Oregon Station method. It is quite evident from this that all soluble material is not taken out by the ordinary official method as outlined in Bureau of Chemistry *Bull.* 107. In all cases here cited it is shown that the amount obtained by the Oregon Station method is nearly double that obtained by the official method. It is possible that in the official method the soluble substances present remained occluded or adsorbed by the arsenate of lead and were not removed by water at room temperature. If, however, successive portions of hot water are used as in the Oregon Station method, this difficulty is overcome and the soluble salts go into solution. In the samples listed in Table I, soluble impurities, in all probability, are composed of chiefly sodium and potassium arsenate since qualitative tests show the presence of these two bases. Other impurities than those found are probably due to impurities in the materials used in the preparation of the commercial arsenate.

Chlorides were found in three of the samples examined. In two of these cases the quantity present was in amounts worthy of note.

The per cent of acid-insoluble impurities in the six samples cited is negligible but these impurities should not, however, be considered an unimportant constituent, as other samples received in this laboratory have shown as high as 5 per cent acid-insoluble material. When present to that extent it is an adulterant of no small consideration.

The tests for the presence of acetates, and sulfates likewise, gave negative results in these six samples.

Other arsenates, analyzed previously in this laboratory, however, have shown that these substances are sometimes present to an extent that would depreciate the value of the arsenate as an insecticide. The detection and estimation of these impurities may be valuable because their presence with the arsenates of lead results in the liberation of water-soluble arsenic oxide.

#### SUMMARY

I—The necessity of more complete methods for the true valuation of commercial lead arsenates has been pointed out.

II—Satisfactory methods have been worked out and applied to commercial samples as follows:

1—Estimation of lead hydrogen arsenate in presence of the mixed salts.

2—The determination of lead carbonate.

3—New methods for water-soluble arsenic oxide and water-soluble impurities.

4—A method for acid-insoluble impurities.

5—The detection of acetates and the quantitative estimation of chlorides.

III—The application of these methods shows a wide variation in the composition of the commercial arsenates and gives a better valuation of them than the methods now in use.

IV—Comments have been made upon the inconsistencies of the Federal Insecticide Law.

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#### A STUDY OF VAPORS FROM DRYING PAINT FILMS

By H. H. KING

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In a recent article appearing in *THIS JOURNAL*,<sup>1</sup> Mr. C. A. Klein, of Middlesex, England, criticized very severely an article communicated by Mr. H. A. Gardner,<sup>2</sup> of Washington. Mr. Gardner's communication contained the result of an investigation as to the "Composition of Paint Vapors."

It cannot be denied that the method of procedure in some instances was open to adverse criticism. Particularly is this the case in the method employed for determining carbon monoxide. In Gardner's method the vapors coming from the drying oil films were conducted first through fuming sulfuric acid, and the carbon monoxide then determined by passing the gases through heated iodine pentoxide. It is a fairly well-established fact that linseed oil films give off formic acid in drying and since fuming sulfuric acid decomposes this acid, setting carbon monoxide free, any conclusion that the monoxide determined has come from the drying films alone must be lacking in absolute accuracy. The point brought out by Klein on this is well taken.

The present writer has been investigating for eighteen months the vapors coming from different drying oils when ground with different kinds of pigments, and had detected very small quantities of carbon

<sup>1</sup> *THIS JOURNAL*, 7 (1915), 99.

<sup>2</sup> *Ibid.*, 6 (1914), 91.

monoxide in such drying films previous to the publication of Gardner's article. Since the appearance of Klein's criticism of this article it has seemed advisable to make known some of the results which have been obtained.

The method of obtaining the vapor for study in the first series of experiments was as follows: A box frame 2 ft.  $\times$  2 ft.  $\times$  4 ft. was constructed of pine, the ends, sides and top of which were made of glass. The floor

with that in which the free iodine was absorbed in potassium iodide solution and titrated with standard sodium thiosulfate.

The vapors were drawn from the drying chamber into towers of standard barium hydroxide arranged to insure complete absorption. The alkali would, furthermore, absorb any volatile acids and retain any aldehydes which may have been liberated. They were then passed through calcium chloride drying

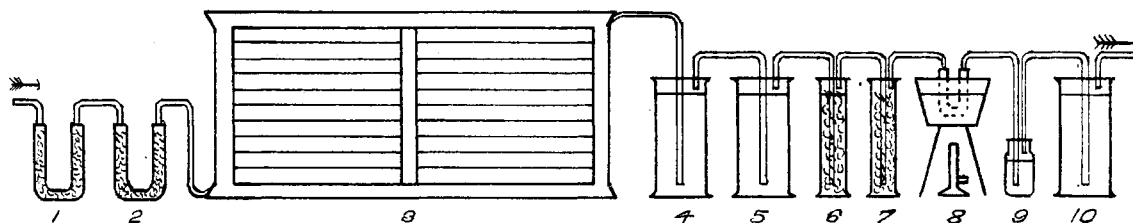


FIG. 1—APPARATUS USED FOR FIRST SERIES OF EXPERIMENTS  
1, 6, and 7—Calcium Chloride  
2—Potassium Hydroxide  
3—Paint Case  
4, 5, and 10—Barium Hydroxide

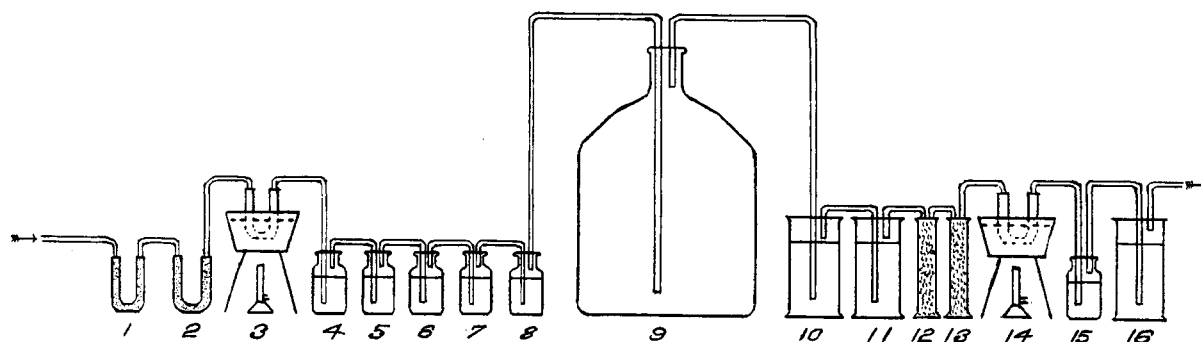
8—Iodine Pentoxide  
9—Potassium Iodide

was coated with melted paraffin well rubbed into the grain of the wood, and the box was made air-tight by the use of a similar procedure. Glass rods fitted into holes bored in the wooden frame on the inside served as supports for eight glass plates about 1½ ft.  $\times$  3½ ft. which were covered with the films by spreading them on with a brush, due account being taken in each case of the amount of both pigment and oil used. In order to insure complete circulation of the air, freed of carbon dioxide by passing through alkalis, it was drawn in at the bottom of one end of this apparatus and out at the top of the other end. In one experiment a small motor and fan were placed inside, but this was found to be unnecessary. The apparatus was then closed and the air drawn through for several hours as a blank test to find if the absorbents or drying chamber gave off traces of carbon monoxide. No evidence of carbon monoxide was obtained.

tubes and finally through a U-tube containing iodine pentoxide mixed with asbestos fiber. The tube was kept in an oil bath at 150° C. The air was drawn from the outside but in this set of experiments no means of removing carbon monoxide was employed because it was deemed unnecessary to take such precautions. Air was drawn through by aspiration at the rate of about one liter per ten minutes. This was done for only about two hours per day on the average.

The films placed on the drying plates were composed of (1) basic white lead and linseed oil, (2) zinc oxide and linseed oil, and (3) a mixture of the two. The percentages of carbon dioxide and carbon monoxide were based on the percentage of the oil employed liberated as the corresponding oxide.

(1) 54 grams of basic white lead in 63.2 g. of oil gave off on drying 20 days, 1.00 per cent of the oil as carbon dioxide and 0.122 per cent as carbon monoxide.



1, 12, and 13—Calcium Chloride  
2—Potassium Hydroxide

FIG. 2—APPARATUS USED FOR SECOND SERIES OF EXPERIMENTS

3 and 14—Iodine Pentoxide  
4 and 15—Potassium Iodide Solution  
5, 6, 7, 8, 10, 11, and 16—Barium Hydroxide  
9—Drying Paint

For some previously conducted investigations on carbon monoxide the present writer had already become familiar with the fact that iodine pentoxide would give off a small amount of iodine on being heated. In order to check this the carbon dioxide formed on passing the carbon monoxide through the iodine pentoxide was absorbed in standard barium hydroxide. It was found that the estimation of the carbon monoxide by this method checked very closely

(2) 86.62 grams of zinc oxide in 144.38 g. of oil evolved 0.60 per cent as carbon dioxide, and 0.0984 per cent as carbon monoxide upon drying 30 days.

(3) 42.12 grams of white lead when mixed with 42.12 g. of zinc oxide, with 84.15 g. of oil, gave off 0.977 per cent as carbon dioxide and 0.118 per cent as carbon monoxide. These films dried 17 days.

These results would indicate that the basic white lead tended to a greater destruction of the oil than

did the zinc oxide, or the lead and the oxide mixed. Later results, however, do not substantiate this.

Another series of determinations were made by the apparatus shown in Fig. 2, the essential differences being in the nature of the drying chamber and the use of a U-tube to take out any carbon monoxide which may have accidentally been present in the air. The drying bottle was a large acid carboy which contained 50 strips of glass plates  $1\frac{3}{4}$  in. wide by 18 in. in length, which were coated and so spaced as to leave their surfaces free and exposed to the air drawn through. A part of the inside surface of the bottle was also coated with the drying films. Tube No. 3 contained fresh iodine pentoxide, while tube No. 14 was an old tube which had ceased to give off any iodine on being heated. The air was drawn through at the same rate as in the other tests.

Runs were made with (1) linseed oil alone and (2) linseed oil and basic white lead.

(1) 23 grams of linseed oil alone gave off 1.05 per cent as carbon dioxide, and 0.13 per cent as carbon monoxide.

(2) 30.21 grams of white lead in 26.79 g. of oil evolved 1.16 per cent of oil as carbon dioxide and 0.108 per cent as carbon monoxide.

In each of the above cases the film dried 15 days.

From these results it would appear that the oil itself gives off about, if not fully, as much of these two gases when drying alone as when mixed with some pigment.

In order to see the effect of sublimed white lead upon the amounts of these two gases set free a third drying chamber was used (see Fig. 3). This was a large cylinder, some six inches in diameter and three feet high, which was filled with carefully spaced glass plates about three or four inches wide and running the length of the cylinder. This was connected to the same kind of arrangement as in Fig. 2.

25.6 grams of sublimed white lead in 35.4 grams of linseed oil set free 0.43 per cent of the oil as carbon dioxide, and 0.047 per cent as carbon monoxide, the films drying during six days.

This would show that sublimed white lead does not differ very much from either of the other pigments used.

In order to ascertain if this evolution of gases continues for a long period of time these chambers have been retained filled with the dried films and will be opened and tested for the presence of these gases from time to time over a period of at least one year.

The evidence points to the presence of carbon monoxide as one of the products given off in the drying of paint films. There is no basis for a statement especially favorable to any one pigment in this respect, as very small amounts of this gas appear to be produced in the presence of all those so far investigated. It is also to be conceded that the amount is so very small that great caution should be exercised in claiming it to be the agent effective as a poison. If the quantity

mentioned in the above results is fairly well distributed with respect to its rate of liberation during the entire drying period of several days, as appears to be the case, no serious danger would be likely to arise in dwellings, as the gas would undoubtedly be too highly diffused and removed too rapidly to cause any harm.

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## PAINTS TO PREVENT ELECTROLYSIS IN CONCRETE STRUCTURES<sup>1</sup>

By HENRY A. GARDNER

The use of protective paints upon metal that is to be embedded in concrete structures, in order to prevent any damage which might be caused by electrolysis, has been heretofore proposed. No tests have been made, however, as far as the writer is aware, which have determined what type of coating is best suited for the purpose. It would appear from first consideration that a paint capable of forming a film of high electrical resistance would be most efficient. Such films, however, generally present a high gloss surface and are apt to prevent the proper bonding of the concrete with the painted metal, thus doing more harm than good. It is chiefly for this reason that engineers have not generally adopted the use of paint upon reinforcing metal. In the experiments presented herein, a method for overcoming this objectionable feature of insulating paints is described, and data are presented on the relative insulating and bonding values of several different types of paint.

**CORROSION CAUSES**—Before describing these tests, it might be well to review briefly, for the benefit of those not thoroughly familiar with the subject, some of the conditions upon which metal corrosion depends. The ordinary forms of iron corrosion have been found to be due to auto-electrolysis, the presence of segregated impurities being responsible for differences in potential at certain areas, which set up galvanic action and cause solution and the formation of rust at the positive nodes. A similar but more rapid action takes place when an electric current is passed through an iron anode immersed in an electrolyte; *e. g.*, salt water. When damp cement contains an embedded iron anode, the cement acts as an electrolyte and the same rusting action takes place, regardless of the fact that concrete contains sufficient lime to inhibit corrosion when no electrical currents are present. With the electrolytic change of metal into oxide comes an increase in volume of the products of reaction, and there is developed an enormous expansive force or mechanical pressure, which is sufficient to crack the strongest forms of concrete.

**SOURCE OF CURRENTS**—Corrosion may therefore be expected, with its attendant results, when sufficiently high-voltage direct currents enter the iron of a new concrete building, either through contact with conductors of light and power circuits, contact with water or gas pipes carrying direct currents from grounded power lines, through defective insulation of electrical wiring, or from similar sources. That the damage is

<sup>1</sup> Presented before the Master Painters' Association of Pennsylvania, Philadelphia, Jan. 12, 1915.

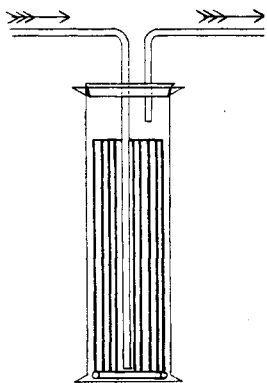


FIG. 3