chloric acid required 8.95 cc. of iodate; the same, plus 1 gram of copper sulphate, required 9.00 cc. of iodate. For the analysis of Paris green, 0.5 gram of the substance is dissolved in 15 cc. of water and 25 cc. of fuming hydrochloric acid, and directly titrated with 5 cc. of chloroform and the decinormal solution of iodate.

Ferrous salts can be titrated in exactly the same way as iodides. Taken: 2.0874 grams ammonium ferrous sulphate. Required: 26.06 cc. iodate, equivalent to 297.6 mg. iron found, or 14.26 per cent. Theory: 14.25 per cent. Unlike the titration with potassium permanganate, oxalic acid does not interfere with thisdetermination. Taken: 2.0843 grams ammonium ferrous sulphate and 1 gram oxalic acid. Required: 25.95 cc. iodate, equivalent to 296.3 mg. iron, or 14.22 per cent. Ferric salts do not interfere with any of these titrations, nor do bromides to any serious extent, if the amount is small. The end-reaction in the titration of ferrous salts is somewhat slow and, in spite of the satisfactory results of the test analyses, is lacking in the sharpness that distinguishes the other titrations described in this paper. This difficulty appears to be avoided by the addition of a small amount of manganous chloride, but the point requires further examination.

The method which has been described is adapted to the determination of almost all the substances to which Bunsen's process of distillation with potassium iodide and hydrochloric acid is applicable, with at least equal precision, with less expenditure of time and far simpler apparatus. It is furthermore applicable in certain cases in which the Bunsen method is not, as, for example, the titration of arsenic or antimony in the presence of copper and ferric compounds.

CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA, May 5, 1903.

THE PERMANENT PROTECTION OF IRON AND STEEL.[1]

BY MAXIMILIAN TOCH.

Received April 14, 1903.

The question of the permanence of modern steel structures, whether the iron and steel used therein is slowly corroding and will in time cause great calamity by the collapse of these structures, has led chemists and engineers to make extensive researches into

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[1] Read before the New York Section of the American Chemical Society.

the stability of iron and steel exposed to atmospheric influence. Both exposed and embedded iron are subject to progressive oxidation under certain conditions, and evidence of this is offered in the record of many cases of rusting of girders and "I" beams of railroad and other bridges, while manufacturers of paints have long endeavored to make a coating of material which would prevent corrosion and oxidation.

The success of such coatings depends mostly upon the skill of the workmen and their proper application. A good paint improperly applied is relatively as poor as a paint of lesser merit. Red lead, for instance, is condemned as often as commended and it is probable that those who have commended it have had it properly applied by skilful workmen under favorable conditions, and then had it covered by better paint. At the same time, it may be regarded as an axiom that it is a blunder to apply a corrosive oxide to a material that will corrode. If a paint be in itself a carrier of oxygen, and the iron or steel be subjected to the action of alternate dampness or dryness or of air charged with carbon dioxide, progressive oxidation is sure to take place and the tensile strength of the metal to be materially reduced. Such conditions may readily occur when a beam is placed in a porous wall. Rapid and continuous oxidation takes place, if steel or iron which is partly rusted is covered with red lead and left exposed.

About fifteen years ago a pamphlet was published in Germany intended to prove that this oxidation is due to electrolytic action, and while the quantity of electricity involved has not been measured, nor positive evidence of it adduced, it seems plausible that such a condition may exist. An iron bar bedding in stone, packed with metallic lead at the point where it enters the stone, always rusts rapidly, suggesting electrolytic action. When two pieces of steel come in contact in a building, rapid oxidation occurs at the point of contact, and this is particularly true of bolt-heads and grill foundation work.

If a clean, pure, cement concrete is packed hard against an iron or steel surface, little or no oxidation can take place, especially if free lime has been liberated in the setting of the cement; but violent oxidation can take place if cinder concrete containing iron oxide, other metallic oxides, free chlorine or any trace of a sulphide be used.

Pieces of anchor chains, which have been embedded in concrete

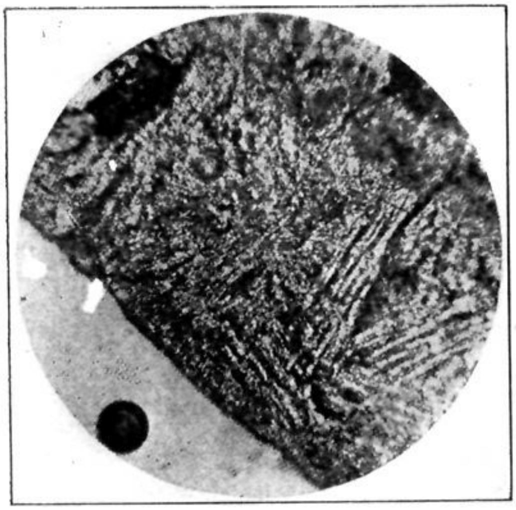

Fig. 1.

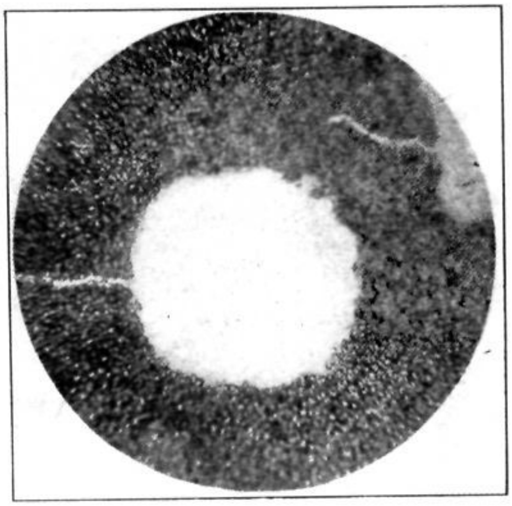

Fig. 2.

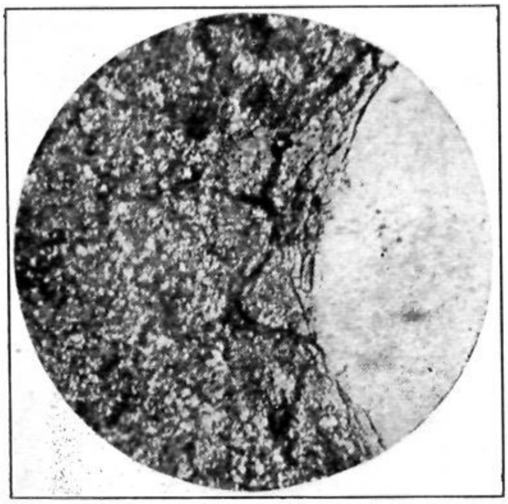

Fig. 3.

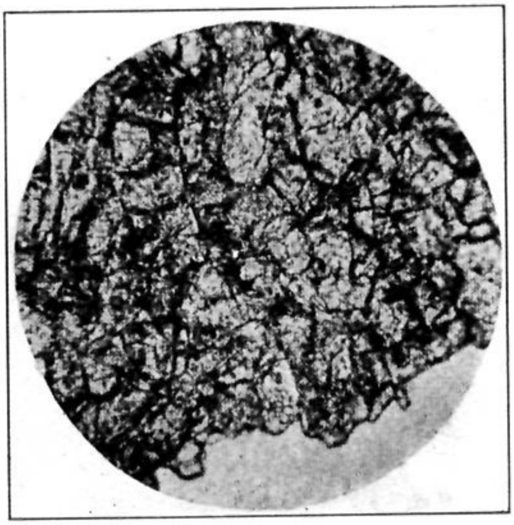

Fig. 4.

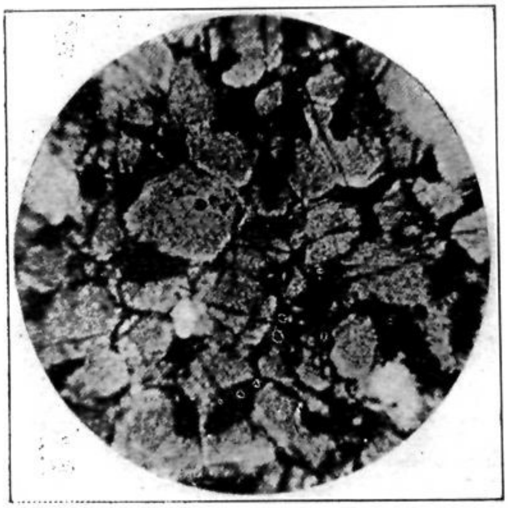

Fig. 6.

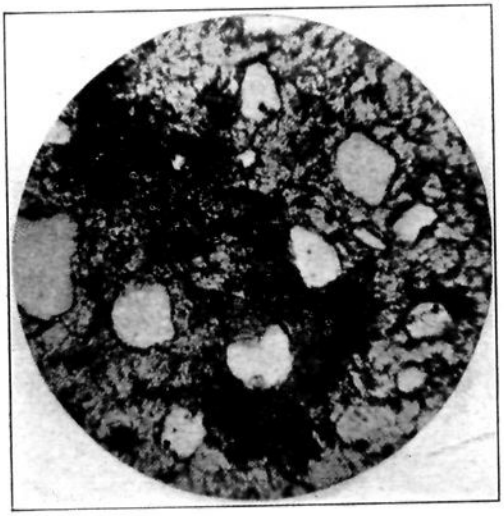

Fig. 7.

Fig. 8.

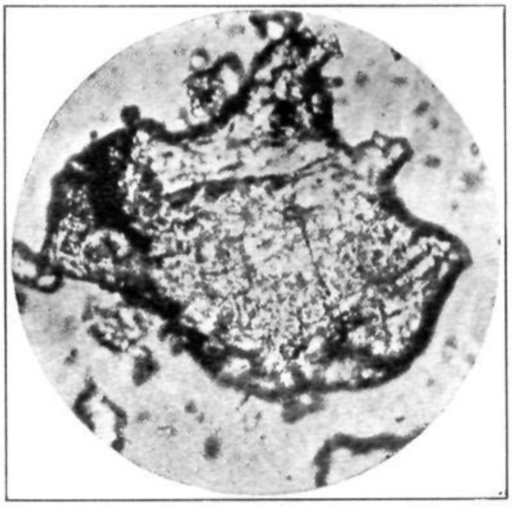

Fig. 9.

Fig. 10.

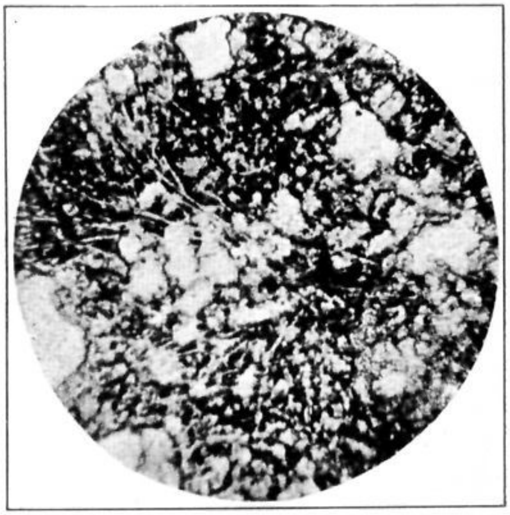

Fig. 11.

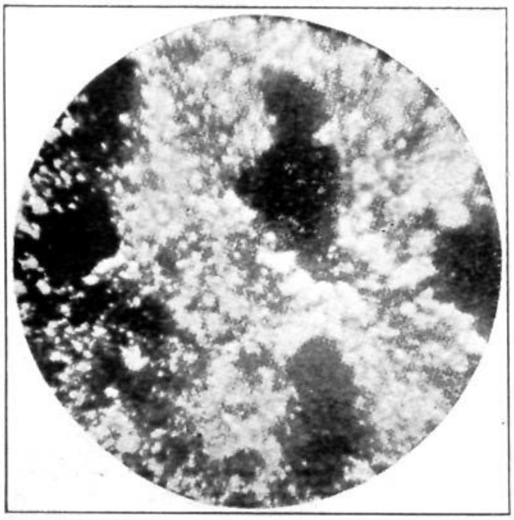

Fig. A.

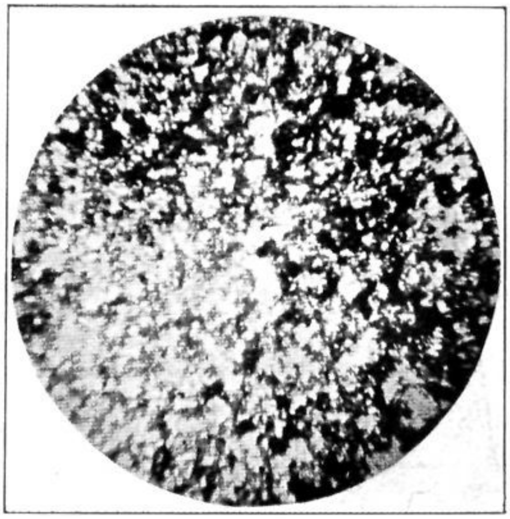

Fig. B.

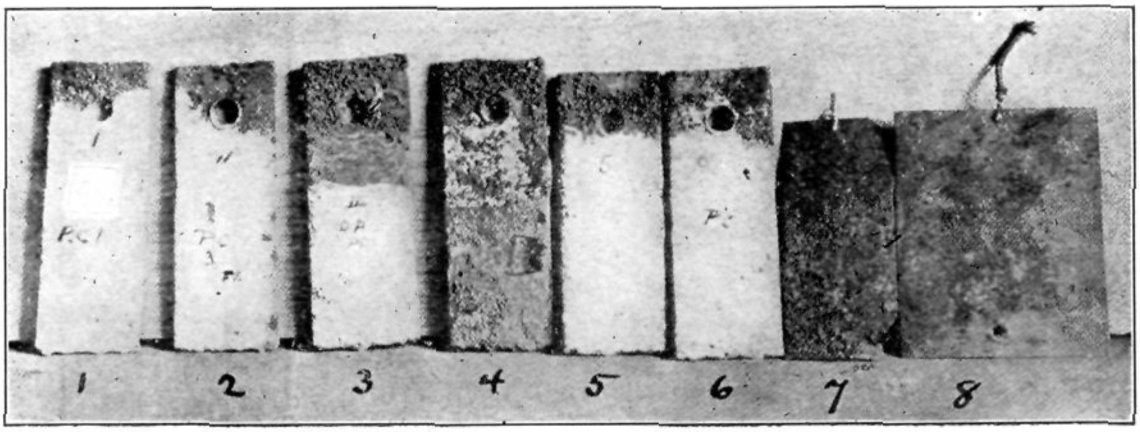

Fig. C.

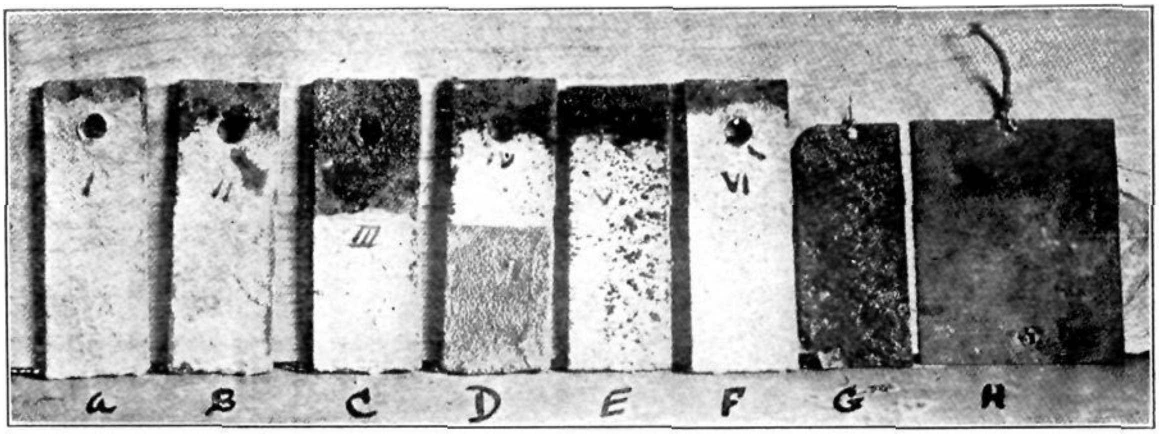

Fig. D.

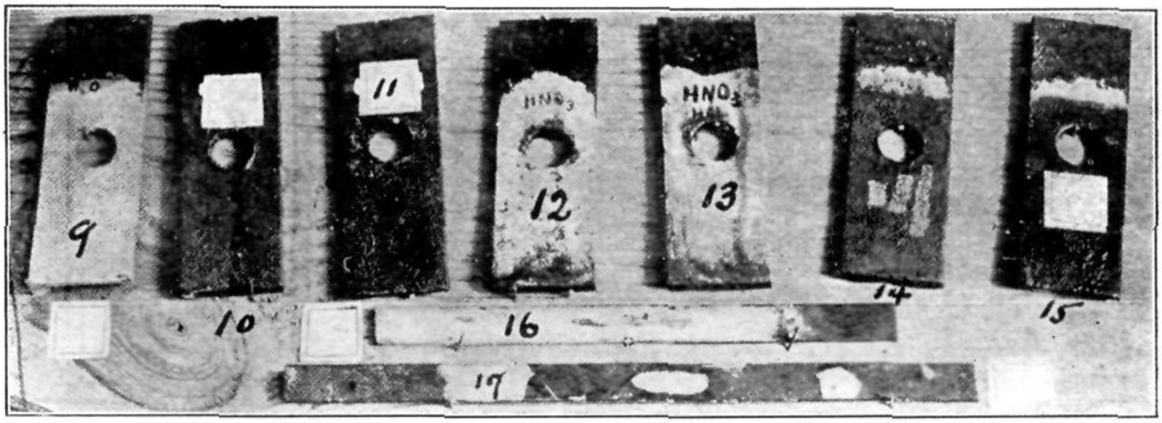

Fig. E.

more than 200 years, have been found in Spain in a state of perfect preservation. Large quantities of metal unearthed in Italy and Greece, extremely old, embedded in cement or concrete, are wonderfully well preserved. These and other observations led me to experiment with Portland cement for the protection of iron and steel against oxidation.

Portland cement, prepared from pure materials in molecular proportions, consists of tricalcium silicate and dicalcium aluminate in a state of solid solution and in the proportion of 85 per cent. of $SiO_2.3CaO$ and 15 per cent. of $Al_2O_3.2CaO$. A Portland cement may also exist in which the aluminate is replaced by dicalcium ferrite, $Fe_2O_3.2CaO$. When such a cement is treated with water, it is decomposed, hydration takes place, and hydrated calcium silicate of lower basicity, combined with an alumina or iron compound, is formed and the product is known as *set cement.* Free lime is liberated at the same time and this explains why linseed oil paint applied to newly set cement is ineffective and why a proper mixture of cement over iron precludes oxidation.

I am indebted to Mr. Clifford Richardson for the use of certain thin sections of typical Portland cements and synthetic compounds prepared to illustrate the structure and physical properties of these important substances. I have made photo-micrographs of these sections which have been reproduced in the following illustrations. In the plates

Fig. 1 represents synthetic $SiO_2.3CaO$.

Fig. 2, synthetic $SiO_2.Al_2O_3.6CaO$.

Fig. 3, synthetic $SiO_2.4Al_2O_3.10CaO$.

Fig. 4, Universal Portland cement clinker.

Fig. 6, Portland cement clinker containing 7 per cent. Fe_2O_3 and no Al_2O_3.

Fig. 7, Celite in Portland cement clinker.

Fig. 8, synthetic $2Al_2O_3.3CaO$.

Fig. 9, synthetic $SiO_2.2CaO$.

Fig. 10, tricalcium aluminate, $Al_2O_3.3CaO$.

Fig. 11, Felite rods in Portland cement clinker.

Fig. A, properly treated Portland cement, finely ground and which sets quickly, magnified 100.

Fig. B, best commercial Portland cement, magnified 100, not fit for paint protection.

To confirm the value of Portland cement for the protection of iron and steel, I prepared cement having the composition above indicated, that is, 85 per cent. of tricalcium silicate and 15 per cent. of dicalcium aluminate, in solid solution with each other. This substance, reduced to fine powder, was mixed with water to a thin paste and applied to plates of steel. The coated plates were subjected to various unfavorable influences, tending to cause them to corrode and rust. About 2 in. of one end of each plate was left uncovered, and this space was in every case badly rusted. When the treatment was completed, the plates were all photographed and the photographs reproduced in the following illustrations.

In the illustrations, Figs. C and D, 1 to 6, and A to F, respectively, represent the same set of plates which were submerged in earth through which was passed, for a period of three months, a current of electricity from a crow foot battery of two cells. The earth was moistened alternately with ammonia, weak nitric acid, and an aqueous solution of ammonium chloride and water. The plates were set in a row, parallel with each other. In the illustrations, Fig. C, 1 to 6 represents the anode sides, and Fig. D, A to F, the cathode sides of the plates.

Fig. 7 represents the plate which was connected with the anode wire and 8, that connected with the cathode wire.

Fig. C, 7, and Fig. D, G show that the anode plate was completely rusted even around the edges, while Fig. C, 8 and Fig. D, H show that the anode plates were much better preserved.

In Fig. C, plate No. 1 was properly treated with pure Portland cement. When removed from the ground it was perfectly preserved and showed no trace of oxidation.

Plate No. 2 was treated with commercial Portland cement containing some metallic iron and calcium sulphate. Marked incrustation of rust appeared under the cement.

Plate No. 3 was coated with an oil paint and afterward covered with cement. It was fairly well protected.

Plate No. 4 was first coated with cement and the latter afterward covered with oil paint. The steel was perfectly preserved.

Plates Nos. 5 and 6 were covered respectively with different samples of Portland cement, the covering of No. 5 being worthless and that of No. 6 excellent.

Fig. E, plates numbered 9 to 17, respectively, were coated with various cement and paint preparations, and subjected to the action of different conditions and reagents. The effect in each case is indicated in the illustration.

Plate No. 9 was coated in the same way as plate No. 1 and for three months was sprinkled with water once a week and allowed to dry. The uncoated portion was badly rusted, but the covered portion was perfectly protected.

Plate No. 10 was coated with cement and an oil paint. Plate No. 11 was coated with cement and a hydrocarbon paint. It was subjected to water and the elements alternately with no unfavorable result.

Plates Nos. 12 and 13 were coated with cement in the same way as plate No. 1 and then supported in a large beaker, the bottom of which was covered with fuming nitric acid. Some of the acid touched the lower end of the plates and lightly corroded them. The uncovered portions were badly corroded, but the acid fumes did not penetrate the cement, and the plates remained in an excellent state of preservation.

Plate No. 13 was subjected for a short time to the influence of fume liberated after addition of hydrochloric acid.

Plate No. 14 was first coated with hydrocarbon oil paint. Subjected during three months to nitric acid fumes, it showed no corrosion under the cement.

Plate No. 15 was prepared in the same way as No. 14 and subjected to the influence of sulphuric acid, carbonic acid and steam; underneath the coating it was thoroughly preserved.

No. 15 is a bar of steel which was coated with a wash of cement of the best commercial grade. The protection was fairly good, but the coating, exposed to wind and rain, was washed off after a few months.

Plate No. 17 was covered first with oil paint and afterward with prepared cement. Roughly handled during eight months, the covering flaked off and the steel was badly corroded.

As a result of the experiments made with the mixture prepared and applied after the manner just described, we may conclude:

(1) If a proper cement paint be applied to a surface which has begun to oxidize, further oxidation will be arrested.

(2) If the cement used be very fine and free from iron, calcium sulphate and sulphides of low specific gravity, it will quickly set on the surface and eventually become thoroughly fixed upon the metal so that rain will not wash it off.

(3) When thoroughly applied, even to three coats, the concrete may be painted with alkali proof and adherent paint, afford-

ing absolute protection to iron so that moisture, carbon dioxide or factory fumes will not penetrate.

(4) Cement paste for application to iron or steel must be made with pure water, and the mixture must be stirred at least fifteen minutes to admit of the liberation of the lime.

(5) Free lime on the surface of the cement coating is quickly carbonated, and then has no injurious action upon linseed oil paint which may, under such conditions, be applied and become extremely efficacious.

The method of waterproofing brick walls from the outside as a protection against penetrating rain or dampness is important in this connection. A newly set brick contains as much as 8 ounces of water, and its power to adhere to the mortar increases with the quantity of water it contains. If a linseed oil paint be applied to a newly erected and wet wall, it quickly peels off and ruins the wall for the further application of paint. But if a proper cement mixture is applied to such a wall in the form of paint or whitewash, it not only adheres perfectly, but forms an excellent base for the application of a good linseed oil paint. Painting the outside wall of a building in this way has some influence on the permanent protection of iron and steel used in construction, since it prevents in a large degree the access of carbonic acid, moisture and gases.

In view of what has just been stated, it is reasonable to believe that structural metal works which have been coated with a layer of cement paint and further protected by a layer of hydrocarbon insulating paint, when embedded in masonry, will be perfectly immune to oxidation and will probably last for all time.

A similar coating affords efficient protection to pipes and conduits placed in the ground and subjected to various influences such as of moist gases, electric currents, acid and alkaline liquids.

Pure Portland cement mixed with water cannot be used as a wash on metal because it will not always set, and it is apt to crack when it does, hence it must be diluted. But care must be exercised that the dilution be not carried too far and the strength of the cement thereby impaired. Voids can be prevented by careful brushing, and for certain structural works where brush work is impracticable, spraying will be effecive. but the cement must then be applied in several layers.

NEW YORK, February 6, 1903.