carbon industry can be had from the patent statistics. During the year 1907, over eighty patents were granted on processes or apparatus using carbon or graphite as electrodes—about 40 per cent. of the total electrochemical patents granted, exclusive of battery patents.

THE DETECTION OF PIN HOLES IN TIN PLATE.

By WILLIAM H. WALKER.

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It is very generally contended among the users of modern tin plate, though not conceded by the makers of the same, that the product now offered upon the market is not so durable as that obtained some twenty years ago. At that time all of our tin plate was imported; but since 1892, or soon after the McKinley Tariff Act was passed, domestic manufacture has steadily grown, until now very little foreign plate is to be found. It is interesting to note that dealers who were previously large importers of tin plate, while maintaining that our present supply is inferior, are willing to admit that even in the "good old times" they were greatly annoyed by the so-called "pin holes" in their goods.

A study of deteriorated tin plate reveals the fact that invariably the tin surface breaks down at a great number of distinct points, and not in continuous patches or zones. The cause of this deterioration is easily seen to be the rusting of the iron (including hereunder steel) base or foundation upon which the tin coating has been placed. These minute bare spots on the iron surface, or small channels through the tin coating down to the iron base are technically called pin holes, and are generally so small as to be undetected by the unaided eye. While unquestionably the number of these holes is greater upon a sheet which carries a very thin coating of tin than upon the triple or quadruple plate, yet upon the heaviest and most expensive plate such as the "dairy stock" used in making large milk cans, the occurrence of these imperfections in the coating is so frequent as to seriously impair the life of the can. Generally the most careful inspection of a heavily coated sheet fails to indicate any lack of continuity of the tin coating, and yet cans made from such stock show rust spots within a few days after being put into service. Contrary to what might be expected, experience demonstrates that the very rough places and apparent imperfections on the bright tin surface are not centers of corrosion, but that rust spots appear at places where the tin coating is seemingly most perfect.

As has already been shown,[1] before iron can form rust it must pass into water solution in the shape of iron ions, and there must at the same time separate from the water or film of moisture an equivalent number of hydrogen ions. Tin is a metal which has a negligible solution pressure, on the one hand, and presents a surface upon which hydrogen can separate and be readily oxidized, on the other. Hence, tin and iron in the presence of water form what is spoken of as a "galvanic couple" or "cell," and an electric current flows from the iron to the tin induced by the solution of the iron and the plating out or precipitation of the hydrogen.

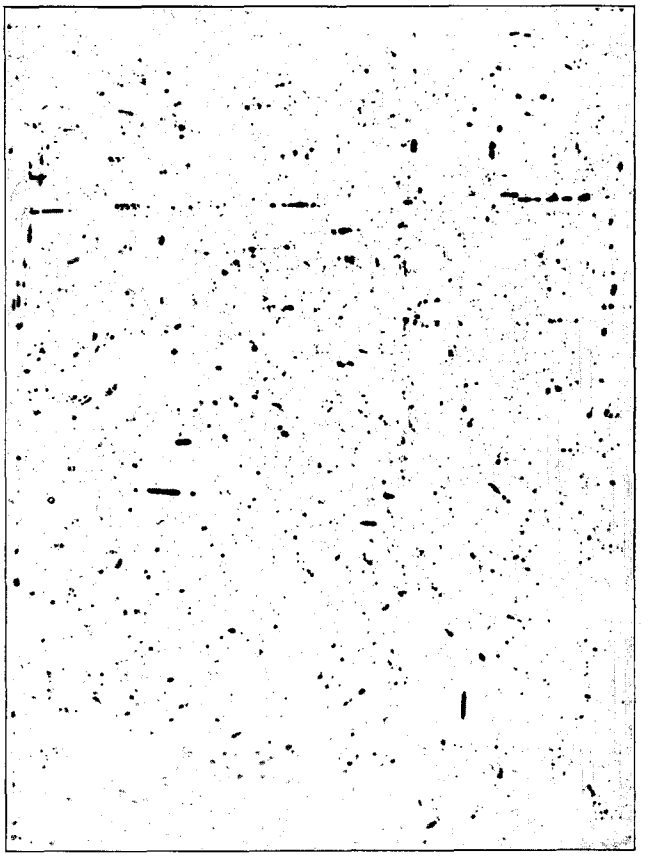

Fig. 1.

In accordance with this theory, when rust spots form upon the surface of a tin plate, the iron must dissolve at the bottom of the pin holes, and pass in this dissolved condition up through the channels to the surface of the tin where it is oxidized by the air and precipitated as rust. But the oxidation and precipitation by the air is not sufficiently rapid to

[1] *Jour. Am. Chem. Soc.*, **29**, 1257.

be easily followed experimentally. Potassium ferricyanide, however (red prussiate of potash), is a reagent which immediately forms with these iron ions an insoluble precipitate and which is bright blue in color. Hence, if at the opening of these

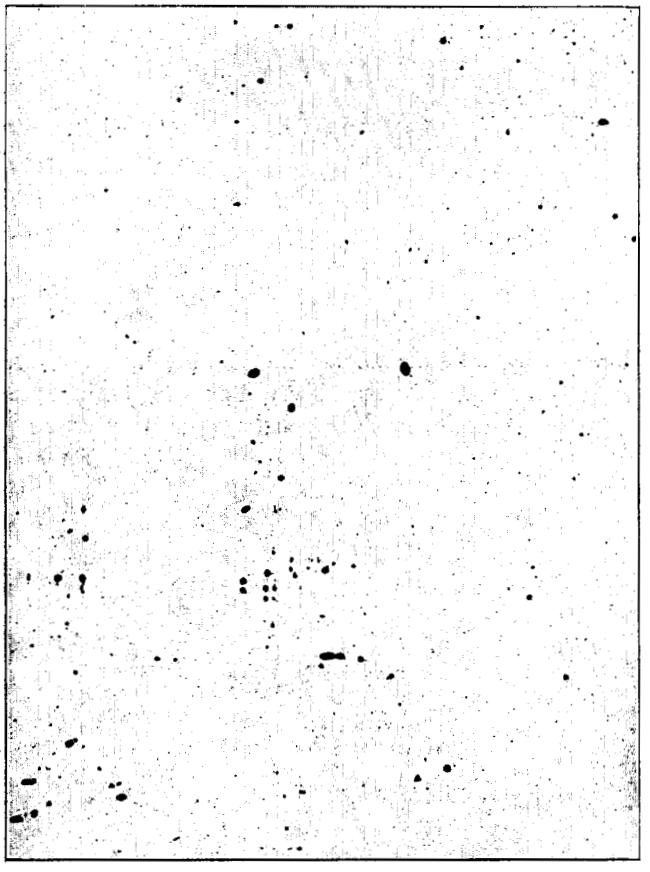

Fig. 2.

channels or pin holes through the tin coating there be a solution of ferricyanide, a blue spot will develop, and indicate definitely the location of the hole. This solvent action of the water can be greatly hastened by increasing the number of the hydrogen ions, which in turn is brought about by the addition of a very little acid. Disturbances on the surface due to convection currents may be eliminated by stiffening the solution with ordinary gelatine. The proportions which have been found to develop the majority of the pin holes within thirty minutes or so, are as follows:

Gelatine	50	grams
Water	450	"
$K_3Fe(CN)_6$	1	"
H_2SO_4	1	"

The gelatine is dissolved in the water by the aid of heat and the ferricyanide added as the reagent is needed; owing to the gradual reduction of the ferricyanide and the action of the acid on the gelatine, the acid should be added only when the gelatine has cooled to about 40° C., and only so much of the reagent prepared as can be used within a few hours. If a large number of plates are to be examined, the sensitiveness of the reaction may be increased by soaking the plates over night in a dilute ammonium chloride solution, or by dipping them for one-half minute in 5 per cent. sulphuric acid. Either of these treatments loosen the material at the bottom of the pin holes, and allows the iron at these points to dissolve more rapidly.

The number and distribution of the pin holes as found upon an average sheet of "coke plate" is shown in Fig. 1, while a sheet of extra heavy dairy stock appears as in Fig. 2. Not infrequently the holes appear to be on lines, indicating that they

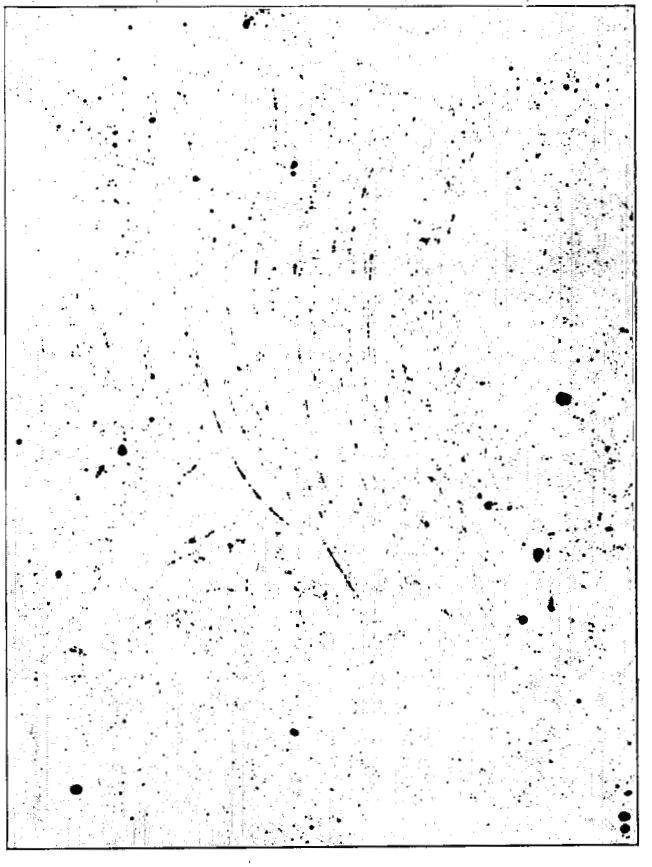

Fig. 3.

may have been caused by a scratch which at places pierced the tin coating, extending down to the iron base. This is well shown in Fig. 3 where the scratches are in curves, suggesting that they were due to the rotating brush used in cleaning the

grease or tallow from the plates, or by moving one plate over another with a twisting motion. Such injuries are seen to be ready centers of corrosion.

In order to determine what proportion of the imperfections brought out by the reagent were due to holes incident to cleaning and handling the plates after tinning, some regular coke sheets were obtained just as they emerge from the tin bath, still covered with the tallow used on the top of the bath. While the number of the holes was reduced, the improvement was not such as to warrant a radical change in the customary method of cleaning. This experiment, however, emphasizes the softness of the tin coating and the great care which must be given to handling tin plate if the centers of corrosion are to be kept at a minimum.

With this easy and accurate method of locating the pin holes or other points on the tinned surface where the iron base is exposed, it is hoped that something more definite may soon be learned regarding the cause of these imperfections and a possible method of preventing them be suggested.

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THE CONSUMPTION OF NITRATE OF SODA IN THE UNITED STATES.[1]

By CHARLES E. MUNROE.

Received March 8, 1909.

On November 10, 1904, I had the honor of calling the attention of the members of the Washington Chemical Society to the fact that as the statistics for the chemical manufactures had come to be taken by the Bureau of the Census they could be made use of in solving many problems of interest and value, provided only that they were properly used, and I pointed out that one of these problems was that of ascertaining the principal industries in which a given material was used and the extent of its use in each industry. The results of this process as applied should prove to be not only of general scientific and economic interest, but also of special value in legislation and litigation where the rule of "principal use" obtains; in determining tariffs and levying taxes; in fixing freight rates; in manufacturing and other operations where the question of substitution may arise; and in other special instances. In the investigation work of the census itself such data furnishes additional checks on the returns.

[1] Read at the Baltimore meeting of the American Chemical Society, December 31, 1908.

The application of this method was illustrated by taking sulphuric acid as an example, since this is the substance of fundamental importance in the chemical industries, and there was presented, in tabular form, the results obtained. These results, after further checkage, have been published on page 23 of "Chemicals and Allied Products for 1905," this being Bulletin No. 92 of that census of manufactures.

Attention having been called to the proper use of the statistics of the census it may be well to state here that, where the chronology is of importance one should be careful to ascertain the period of time to which any given census statistics refer, because, in a census of manufactures, the data record transactions already completed at the time the investigation was made, and, because of changes in the law, as enacted by the Congress, the yearly periods covered may not be similar and the intervals between the successive censuses may not be of precisely the same length. In illustration we have the census of 1900, covering the operations for the year ending May 31, 1900, and the census of 1905, covering the operations for the calendar year ending December 31, 1904, except for the State of Michigan, where, for the purpose of coöperation with the State authorities, and to avoid duplicate enumeration in the same year, the statistics were collected for the year ending June 30, 1904.

Also it may be proper to point out the chance of error which may arise from making use of census data without consulting the text carefully so as to ascertain to what the data applies. Thus, if one wishes to obtain the statistics for the chemical industries of this country at the census of 1905 he might consult Table CX on page clxxi, of Part I, and find the value of the products given as $1,031,965,263, or he might consult Table 1, on page 398 of Part IV and find the value of the products given as $323,997,131 or a difference of over $707,000,000 in the value of products for the same period of time. But on investigating the tables and their accompanying text we find the first to cover the "Chemical Group" and to embrace a large part of those substances found in chemical technologies, while the second table treats only of those substances styled in the census classification, "Chemicals and Allied Products." Also, to take another example, we find from Table 8, page 404 of Part IV, that the sulphuric acid produced at the census of 1904 was 467,614 tons, while from Table II on page 405 of the same part, the sulphuric acid