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CITATION:

SAWAI, Ikutaro ...[et al]. The Effects of the Pickling Process on the Amount of Hydrogen Occluded in Steel Plate for Porcelain Enamel. Memoirs of the Faculty of Engineering, Kyoto University 1951, 13(2): 70-76

ISSUE DATE:

1951-03-31

URL:

http://hdl.handle.net/2433/280230

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By

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(Received February, 1951)

Introduction

As early as 1919 Treishel[1] pointed out that the conditions of cleaning process in the porcelain enamel industry affect strongly the liability of the occurence of the defects such as blisters and fish scales. He, and also other authors, for example, Deutsch[2] suggested that hydrogen absorbed in steel during the pickling process may be the source of defects. Later, Zapfe and Sims[3] succeeded to demonstrate the effect of hydrogen. Their so called "hydrogen theory" states that a part of hydrogen absorbed in steel plate during the pickling process is very difficult to be removed especially with thicker plates, because the atomic hydrogen dissolved in the texture diffuses exceedingly slow at room temperature and the molecular hydrogen occluded in cavities does not split into atoms at the lower temperature than 800°C, hence the remaining hydrogen which tends to escape later will become the main source of defects. To give the positive evidence their experiments were carried out for extreme cases, for example they used as samples the wedge of plain steel to demonstrate the effect of thickness and the plates bored and sealed by plug to prepare the artificial cavities. Although the results could verify their theory so well in principle but the conditions are too far apart from the factory practice as to be taken as standard for the actual pickling process, moreover they have not determined the real amount of hydrogen.

Therefore the authors have intended, by means of micro gas analysis, to find out the relations between the amount of remaining hydrogen and the conditions of the cleaning treatments such as washing, drying and neutralizing, and also the thickness and the cavities of plates. In addition, using the steel plates of 0.56 mm and 6.0 mm thick, which are generally used among our firms, the present experiments have been scheduled to represent, as far as possible, the factory conditions.

Experiment

1. The Method of Analysis.

For the determination of hydrogen in steel the vacuum heating procedure was used. This process is, in principle, to collect and analyse the gases evolved from sample exposed to high temperature under vacuum.

The whole equipment[4] is composed of an electric tube furnace for heating the sample, being enclosed in a fused silica tube of 550 mm long and 20 mm in diameter, up to 800°C, a set of a mercury diffusion pump and mercury pump of Beutel type used for the purpose of collecting and carrying the gases to an accumlater by holding them between the circulating mercury drops, and an apparatus for micro gas analysis of Ambler type.

The apparatus was evacuated to 5×10^{-4} mm Hg or less before the sample will be heated. By blank test it was confirmed that hydrogen in steel can be extracted perfectly by heating for 30 minutes at 800°C under vacuum, but, for the accuracy at present the heating was scheduled to 60 minutes. The leakage during this period was found to be less than 0.08 cc.

The plates were subjected to the pickling, the after treatments under various predetermined conditions, the after cleansing snccessively by alcohol and ether, dried in an air bath for three minutes at 70°C and then stored in a quatz tube.

The chemical composition of the steel plate was C: 0.06, Si: 0.05, P: 0.06, S: 0.04, Cu: 0.32%, an item which is generally used by the Japanese enamel factories. Thin plates of the thickness of 0.56 mm and those of 6.0 mm thick have been used for the present experiment.

2. Preparation of Samples.

A. Samples for the Investigation of the Effects of the Methods of Washing and Neutralization.

From a steel plate of #25 (0.56 mm in thickness), which had been confirmed as to be able to produce the enameled ware free from defects such as blisters by regular cleaning treatment, 420 pieces of 60×10 mm plates have been cut off, and after randomizing divided into seven equal parts, subjected to the following different treatments:

(a) surface is polished mechanically until the black scale completely disappears.

(b) after being heated for three minutes at 600°C the samples are pickled in the 10% sulphuric acid solution of 70±5°C for 10 minutes, washed by water for two minutes, neutralyzed by the 3.5% sodium carbonate solution of 70±5°C for 10 minutes and again washed for two minutes.

(c) after pickled with the sulphuric acid solution, simply washed by water for 25 minutes.

(d) after pickled, treated by boiling water for 10 minutes.

(e) after pickled, washed by water for 25 minutes, neutralyzed by the 3.5% sodium carbonate solution at room temperature for 5 minutes, washed by water for two minutes.

(f) after pickled, neutralyzed by 3.5% sodium carbonate solution at room temperature for 25 seconds, washed by water for two minutes. The samples processed according to the schedule classified above will be named hereafter as A-a, A-b, A-c, A-d, A-e and A-f, in which the letters A indicate the kinds of investigations and small letters correspond to different procedures. The schedule A-b is the normal factory process for cleaning while those of A-c to A-f correspond to the cases in which the treatments after pickling are modified or simplified. The washing was done by running water at room temperature. Chemically pure sulphuric acid was used for the present experiments, and the solution was renewed after treating 8 pieces (about 22 grams) which are used for single analysis. In order to avoid the unnecessary storage of samples the whole procedure, from annealing to gas analysis, bave been carried out in the same day.

B. Samples for the Investiation of the Thickness of Steel Plate.

From a steel plate of 6.0 mm thick, which was confirmed as to be able to produce enameled ware free from defects by regular cleaning treatment 10 pieces of 60×10 mm plates were cut out. After randomizing they were divided into halves. One of them was cleaned according to the schedule "b" of the preceding section and the other was simply polished.

C. Samples for the Investigation of the Effect of Cavities.

For a test piece with cavites a 60×10 mm plate was cut out from a # 25 steel plate having blistered spots so that it contains five blisters of 1 mm in diameter. Blisters had occured in annealing process. To remove gases, mainly composed of hydrogen, the test piece was heated under vacuum for 60 minutes at 800°C. It was then pickled with 10% sulphuric acid for 15 minutes at 70±5°C, washed for 25 minutes by water and dried for 3 minutes at 70°C in an air bath. With the same test piece another two series of experiments were made variating the time of drying to 15 and 60 minutss. According to the time of drying the above three kinds of samples, will be named as C-3, C-15 and C-60 respectively. In order to remove the residual gases completely the test piece had been heated under vaccum for 60 minutes at 800°C before it was submitted to the next experiment.

3. Results.

The results of the analysis of hydrogen are summarized in the Table 1 to 3.

To facilitate the comparison all figures in the tables are reduced to the volume of hydrogen in cc. at n. p. t. evolued from 100 grams of samples.

Table 1.

Method of cleaning	Volume of Hydrogen in cc.						
	1	2	3	4	5	6	7
A-a	2.17	2.73	3.37	1.60	2.07	3.21	3.42
A-b	2.29	3.28	4.62	2.65	2.67	4.43	4.39
A-c	4.26	3.89	2.74	4.61	4.37	3.63	—
A-d	2.96	2.98	3.86	4.67	4.88	5.03	—
A-e	3.40	3.54	2.74	4.38	4.74	3.26	—
A-f	5.03	5.41	4.01	3.45	3.22	4.71	—

Table 2.

Method of cleaning	Volume of Hydrogen in cc.				
	1	2	3	4	5
B-a	0.42	0.62	0.34	0.46	0.51
B-b	0.88	1.20	0.93	1.07	0,89

Table 3.

Method of cleaning	Volume of Hydrogen in cc.		
	1	2	3
C-3	18.87	18.85	17.98
C-15	11.47	9.94	10.21
C-60	10.27	9.73	9.46

Discussion of Results

As we can see in the preceding tables the fluctuations of the results of analysis are so large that it seems to be difficult to draw any conclusion. This certainly comes from the influence of the accidental variations of some factors which can not be controlled even if the greatest care is taken to adjust the conditions of cleaning procedure and the estimation of hydrogen. The following statistical treatment may help the interpretation.

By means of the "Method of Student's t Test" the comparisons have been made between A-a and A-b, A-c, A-d, A-e, A-f respectively of the Table 1, between B-a and B-b of the Table 2, between C-3 and C-15 or C-60, between C-15 and C-60 of Table 3.

The mean values of the samples, the difference of mean values $|\bar{x}-\bar{y}|$ and the values $D_{0.05}$ are tabulated in Table 4, in which $\bar{x}$, $\bar{y}$ represent the mean value of samples $x_1, x_2, x_3, \ldots\ldots, x_n$ and $y_1, y_2, \ldots\ldots y_n$ obtained from two sets of measurements and the values $D_{0.05}$ are calculated by the equations

$$D_{0.05} = t_{0.05}(\phi)\sqrt{\frac{1}{n_x}+\frac{1}{n_y}}\,\sigma\,,$$

$$\sigma = \sqrt{(S_x+S_y)/\phi}\,,$$

$$\phi = n_x+n_y-2\,,$$

where S_x, S_y are $\sum_{i=1}^{n}(x_i-x)^2$, $\sum_{i=1}^{n}(y_i-y)^2$ and n_x, n_y the numbers of samples of x and y, respectively, and $t_{0.05}(\phi)$ is the costant when the significant level is taken as 5%.

Table 4.

	Mean values (Vol. of Hydrogen in cc.)	Comparison	$\lvert\bar{x}-\bar{y}\rvert$ $D_{0.05}$	Remarks
A-a	2.65	—		
A-b	3.48	A-a	$0.83 < 1.02$	significant at the levle of 20% ($D_{0.2}$=0.81)
A-c	3.92	A-a	$1.27 > 0.84$	
A-d	4.06	A-a	$1.41 > 1.02$	
A-e	3.68	A-a	$1.02 > 0.96$	
A-f	4.31	A-a	$1.66 > 0.97$	
B-a	0.47	—	— —	
B-b	0.99	B-a	$0.52 > 0.18$	significant at the level of 1% ($D_{0.01}$=0.26)
C-3	18.57			
C-15	10.54	C-3	$8.03 > 2.27$	
C-60	8.82	C-3	$8.75 > 1.60$	
C-60	9.82	C-15	$0.72 < 1.47$	

By comparing the values of $|\bar{x}-\bar{y}|$ and $D_{0.05}$ we can drawn the following conclusions.

1. The difference between A-a and A-b is not significant at the level of less than 5%, or in the other words, we can not assign the statistical meaning for the difference of both figures if our judgment should be correct as far as 95%. First at the level of 20% the above difference become significant. Therefore we can conclude that with the thin plate of 0.56 mm thick the hydrogen in steel absorbed during the pickling process will be removed almost perfectly if the neutralization and washing procedures are carried out according to the normal schedule such as

A-b, and the hydrogen content will become as low as that of the mechanically polished sample (A-a).

2. The mean values of $|\bar{x}-\bar{y}|$ and $D_{0.05}$ between A-a and A-c, A-d, A-e, A-f respectively are in the same order, but in these cases $|\bar{x}-\bar{y}|$ are always a little larger than $D_{0.05}$ so that the differences become significant even at the level of less than 5%. This means that even with the plate as thin as 0.56 mm the departure from the normal schedule (A-b) in the aftertreatment may be the cause of the accumlation of hydrogen in steel. The mean value of hydrogen content in this case is about 3/2 of A-a.

3. With the thicker plates the difference $|\bar{x}-\bar{y}|$ and $D_{0.05}$ becomes significant at the level of as low as 1%; e. i. with the plate 6.0 mm thick the hydrogen can not be removed even if the after treatment is carried out according to the mormal procedure and consequently the hydrogen content becomes by far larger as compared with the polished sample (B-a). The mean value of hydrogen content of B-b is twice as much as that of B-a.

4. The hydrogen content of the sample C-3 was found to be as 17~19 cc and is about four times of that of A-c. The difference of the hydrogen contents of C-15, C-60 and that of C-3 are significant at the level of less than 5%. Moreover the comparison of the mean values indicates that the hydrogen absorbed in cavities can be reduced to about half by heating the samples at 70°C. However the comparison between C-15 and C-60, the difference of those is not significant at the level of less than 5%, indicates that, by heating at 70°C, the amount of absorbed hydrogen decreases at first rather rapidly and then, after it has reached to a certain value, does not change apparently by the continued heating at the same temperature.

Summary

By direct estimation of the hydrogen content in the enameling steel of the composition C: 0.06, Si: 0.05, Mn: 0.44, P: 0.04, Cu: 0.32% by vacuum heating procedure the authors have confirmed the following facts.

(1) The hydrogen absorbed in steel plate of 0.56 mm thick during the pickling with 10% sulphuric acid solution will be removed almost completely if the aftertreatment will be carried out according to the normal schedule. However, with the plate of 6 mm thick a part of hydrogen will remain obstinately even if the after treatments are strictly obeyed to the normal schedule.

(2) If the schedule of after treatment will be changed arbitrary or be simplified then a part of absorbed hydrogen may remain in steel plate so thin as 0.56 mm.

(3) A large quantity of hydrogen will remain in steel plate especially when

the latter has cavities, and a part of hydrogen accumlated in holes can not be removed by the prolonged heating at 70°C.

Acknowledgment

The authors are indebted to the financial support of the Ministry of Eduction given for the present investigation and also to T. Nishioka for his assistance in the gas analysis.

References

1) C. Treishel, J. Am. Cer. Soc., 2 (10), 1919, 774-81.
2) B. Deutsch, Enamelist, 17 (12), 1940, 6.
3) C. A. Zapfe and C. E. Sims, ibid., 23 (1), 1940, 137-219.
4) The apparatus is similar to that enacted by the 19 th Sectional Committee of the Japan Society of the Promotion of Scientific Research (Tetsu to Hagane, 25, 1939, 413).