

The Effect of Adding Small
Percentages of Finely Ground
Metals to Enamels

by Glenn L. Pyle

May 15th, 1912

Submitted to the School of Engineering of the
University of Kansas in partial fulfillment of the
requirements for the Degree of Bachelor of Science

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TO ENAMELS

GLENN L. PYLE

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Glenn L. Pyle.

Lawrence, Kansas,

May 15, 1912.

Professor H. P. Cady,

University of Kansas,

Lawrence, Kansas.

Dear Sir:

I hand you the following thesis required for the Degree of Bachelor of Science, in the Chemical Engineering Course of the University of Kansas. The subject of this thesis was suggested by Messers Brock and Weith and the experimental work was done under their supervision.

Yours sincerely,

Glenn L. Pyle.

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PREFACE.

The work of this thesis was done at the University of Kansas in the Department of Industrial Research. The subject of the thesis was suggested by Messers Brock and Weith and the experimental work was done under their supervision.

The thesis was written for the Degree of Bachelor of Science and most of the experimental work was done during March, April and May of 1912.

The final work of the thesis was submitted to Professor H. P. Cady, Director of the Department of Chemistry, and was approved by him.

THE EFFECT OF ADDING SMALL PERCENTAGES
OF FINELY GROUND METALS TO ENAMELS.

The object of this thesis was an attempt to prevent the formation of pin holes in the process of enamelling on steel.

By enamel is meant a vitreous substance applied to steel or iron for protective purposes only and not for decorative effect. Enamels are commonly a double silicate with oxids of the alkalies and oxids of the heavy metals. The raw material used in the manufacture of enamels are silica, silicates, boric acid and borates, carbonates and oxids of the alkaline earth group, carbonates of the alkali group, metallic oxids, and decoloring agents. Generally speaking to resist acids well an enamel must have a high acid content. This as a general rule is accomplished by increasing the per of silica, and as a result raising the fusion point of the enamel. To lower the fusion temperature lime, alkalies, borates and fluorids are added. For using metallic oxids various reasons are given. It seems to be a fact that the heavy metals increase the resistivity

of an enamel against chemical action. Cobalt oxid aids the enamel to stick to the iron or steel and is therefore usually used in ground coats. There are two methods of applying enamels;

(1) To grind the fused fritt to a fine powder and then dust this dry powder through cloth bags onto the dampened surface of the iron or steel.

(2) To grind the fused fritt with a certain percentage of water and clay, to a thin gruel-like consistency and then to dip or slush this material over the surface of the iron or steel.

Each of the above methods has its own advantages for certain classes of work.

One of the greatest, if not the greatest, trouble in the enamelling industry is probably caused by the small pin holes which form in the enamel while it is fusing down on the metal. If the enameled vessel is used to hold an acid liquid the solution soon works down into these minute holes, eats out the metals, and causes the enamel to chip away from the steel surrounding the pin holes.

There may be various causes for the formation of these small holes in enamels but the cause is generally attributed to the reduction of some of the constituents of the enamel by the carbon

of the steel.

It has been proved by various experimenters that steel reduces metallic constituents of enamels and there is no reason to suppose that graphite will not do the same thing.

Table No. 1. shows some preliminary experiments on this point. The plates used were of porcelain, from an evaporating dish, and platinum, an ordinary platinum crucible lid. The table shows that very few bubbles were formed in these cases, and this is taken as an added proof that the bubbles are caused by a gas or by gases.

TABLE No. I.

No. Plate.	No. Enamel.	Percentage metal.	Time			Temperature.	
			B	E	D	B.	E
Porc. #1.	91	0.1 Alumin.	2:30	2:33	3	820	830
" " "	"	0.1 "	"	"	"	"	"
" 2	"	0.1 "	2:37	2:40	"	810	820
" 2'	"	0.1 "	"	"	"	"	"
" 3	"	0.1 "	2:45	2:48	"	820	840
" 3'	"	0.1 "	"	"	"	"	"
Platinum	91	0.1 "	3:00	3:03	"	820	810

REMARKS.

Porcelain #1 & 1' - transparent, no bubbles.
 " 2 & 2' - a few bubbles, yellow color.
 " 3 & 3' - transparent, no bubbles.
 Platinum 1. - two small bubbles at bottom.

After these experiments it was taken for granted that carbon monoxid and carbon dioxid gases were formed in the process of enamelling. It was also presumed that one of these gases was

the cause of the blisters and bubble holes in the enamel.

The literature on the subject of enamels and enamelling is not very extensive, and the subject of pin holes is rarely mentioned or discussed in books or magazine articles. Rudolf Vondracek says that only in the enamelling of iron is there any trouble on account of bubbles and that on pure metals, such as gold and silver, the enamel is compact and free of blisters, etc. Pure electrolytic iron acts like gold and silver. Mr. B. Kerl says that if one wishes to melt an enamel colored white with tin oxid direct on iron the white color would suffer on account of the reducing effect of the carbon of the iron upon the tin oxid, and the enamel would be rendered porous on account of the evolution of the oxide of carbon. Other substances also are reduced by the carbon of the iron and cause an evolution of gas. The problem will then resolve itself into two parts: either to prepare the enamel so that the carbon of the iron will not reduce the constituents of the enamel at the temperature at which the enamel is fused onto the iron, or to prepare the metal in some way so that the effect of the carbon is removed.

The last method is the one most generally used. There are several ways of applying this

method. The most common one is the application of a ground coat before the final enamel is put on.

The ground coat also performs other functions for instance in neutralizing the expansive effect of the steel on the top enamel. Some think this the only use but P. H. Eyer says that in covering sheet iron with an enamel a ground coat must be put on first which is to prevent the reduction of the metallic oxids in the enamel by the carbon of the iron.

This method is used almost entirely in the enamelling of cooking utensils and sign enamelling. This ground coat must fuse at a higher temperature than the final coating and must contain no substances that would react with the top layer or finish coat. Other neutral layers have been tried but without much success. Electrolytic iron and copper plating have been tried but the deposits do not stick well. Rudolf Vondracek says that he got good results by heating for fourteen hours a cast iron vessel with ground up iron oxid, to a red heat. He sprinkled the enamel on this oxid layer in the ordinary way and got an enamel free from bubbles. Experiments carried out by Messers Weith & Brock have shown this method to be of very limited application and at the best does not give very satisfactory results. A patent has recetly been issued for the removal of the carbon

by means of sulphur. The sulphur is simply sprinkled on the steel and heated. The reaction would result in the formation of carbon bisulphid. No information is at hand in regard to the results obtained by the use of this method. A method used to some extent is heating the steel in the open air before enamelling. This helps some but does not free the metal entirely of carbon.

The second method of preventing the reduction of the enamel by the carbon, e.g., regulating the composition so that the carbon in the steel will not react with the enamel constituents, is one most commonly used. There is no scientific method for using this method, however, and all enamel formulae are mostly empirical. Another way of attacking the problem in this way is to apply a very fusible enamel to the red hot iron. The enamel in this case melts on the iron so quickly that the reduction process does not take place to any great extent and therefore tends to prevent the troublesome bubbles.

The method purposed to use in these experiments is a modification of the second process just described. It was reasoned that if a reducing agent could be put into the ground enamel before application that the gases coming off from the steel would be reduced and in this way prevent the gas from coming to the surface and forming

bubbles. It was recognized that there would also be a reducing effect on the metallic content of the enamel. The iron itself has a reducing effect on tin oxid and lead oxid in the enamel. This has been proved by M. Mayer and B. Havas in a series of recent experiments.

This fact was, however, left out of the problem for the time being and only the possibility of the gases being reduced taken into consideration. In selecting our reducing agent two points must be observed;

(1) The reducing agent must enter into combination with the enamel in such a way as not to harm its properties.

(2) It must not form a gas at the temperature of fusion of the enamel.

The only substances thought to fit these conditions were the heavy metals. Four metals were chosen, namely, aluminum, magnesium, zinc, and copper. They were very finely ground.

An enamel was selected from the list of experimental enamels of Weith & Brock. One was picked out that melted at a medium temperature, did not contain many heavy metallic oxids because of the reducing effect of the adulterated enamel, and one that contained a medium number of bubbles and pin holes. The formula for an enamel suitable for the work was as follows:

SiO₂ = 34.7%

Al₂O₃ = 4.0"

Na₂O = 33.0"

B₂O₃ = 5.0"

TiO₂ = 23.3"

This enamel was numbered 91, and was made from glass sand, feldspar, sodium carbonate, borax, and rutile.

The description of the enamel as given by Weith & Brock in their experimental work, is as follows;

Color- Transparent yellowish brown to reddish brown, the color depending on the time and temperature.

Lustre- Dull to glossy.

Opacity- Transparent.

Structure- Bubbles and pin holes, worse with rise in temperature. Also crazing.

Burning- Burned on first plate around edges due to viscosity or too thick a coat.

Stickability- Fairly good. None of the plates were good.

A few experimental plates were run and the results obtained compare very favorably with the above description of the enamel.

EXPERIMENTAL PART.

PREPARATION OF MATERIALS AND ENAMEL.

The metal plates used in these experiments was hoop iron. Hoop iron is a low grade cheap steel and was selected because it was readily available and was thought to compare favorably with the steel used in actual practice. The steel was cut into plates 1-1/2" X 3/8" X 4". The plates were cut four inches long because it would make them just the right length to put end to end in the furnace. Thin steel was selected so that the plates would soon become heated when placed in the furnace. After being cut to the proper size the plates were numbered with steel dies in consecutive order from 1 to 150. In order to remove the rust and other foreign matter from the plates they were pickled in acid.

Pickling consists in immersing the plates in a dilute acid. In this case the steel was placed in a rather large jar and a 10% solution of sulfuric acid poured upon them. They were stirred around with an iron rod until plates taken out and scrubbed with a steel brush showed

a bright clean surface free from rust and mill scale. The plates remained in the acid about an hour before the rust was all removed. At the end of that time the acid was poured off and the steel washed. After thorough scrubbing with a steel wire brush the plates were dropped in slacked lime to dry. The plates were not allowed to remain in the air for any length of time as a coating of rust formed in a very short time. The lime served the double purpose of neutralizing any acid which had escaped the washing, and of absorbing the moisture. After remaining in the lime for about an hour the plates were taken out, most of the lime sticking to them, removed by knocking them against the side of the lime box, and placed in a dessicator for future use.

The enamel was prepared by weighing out the fluxes on a flux balance, putting them together in a dish, stirring well, and finally grinding thoroughly in a an Abbe ball mill. They were ground to almost an impalpable powder. , The time taken in grinding was about forty-eight hours. The ground fluxes were now put a little at a time into a crucible which had been previously heated in a pot furnace fired with natural gas an air. The temperature of the pot furnace was estimated at about 1200° C. Although no exact measurements were taken it is safe to assume this temperature

to be approximately correct. The enamel bubbled a good deal while melting down due no doubt to the use of carbonate. The fluxes were allowed to fuse together until they melted to a quiet liquid. In order to tell whether all the particles were in solution or not, an iron rod was thrust into the molten enamel and stirred around until a small gathering was made on the end of the rod. The liquid enamel was allowed to run down in a fine string and the thumb and finger moved along the fine string of glass to feel any lumps of undissolved material. If the string of enamel was smooth and even the enamel was considered done and was poured into a pail of water which cooled and granulated the molten glass.

Half of the enamel fritt was now taken and ground again in the ball mill as before. The other half was saved to be ground with the pure metals. The unground fritt was used in preference to the ground as it was thought that perhaps the rough edges would help the mixing of the metal with the fritt. The un-ground fritt was weighed out one hundred grams at a time and 0.1%, 0.5%, and 2.5% of each of the metals were mixed with the separate batches in secession. These mixtures were put away in bottles and ground together as time allowed throughout the experimental work. They were ground in a mechanical agate mortar, similar

to the McKenna grinder. They were all ground very fine, almost to an impalpable powder. The metals used were all ground very fine and were pure. It was feared that some of the metals had been ground in oil and so they were thoroughly washed with ether to remove any oil or grease that might be present.

Everything was now prepared and ready for actual enamelling. The furnace used throughout this work was a natural gas muffle furnace built by the American Gas Furnace Co. The muffle was about 10" X 18". A Le Chatelier pyrometer was used in determining the temperature. The silica tube was placed in a small hole in the back of the furnace and was supported in the middle by a cupel turned up side down. Three cupels were placed 4" apart side by side in the muffle near the end of the silica tube. These were used as supports for the plates during firing. The cold junction of the pyrometer was placed in water and no attempt was used to keep it at 0°C. since it would require so much care and would only make a few degrees difference in temperature. The wires from the cold junction were run to the binding posts of a millivoltmeter. The wires and binding posts were carefully cleaned and sandpapered lightly each time in order to be certain of getting good electrical connections.

The process used in enamelling was as follows. Two small shaving powder boxes were taken, and in one was placed the ground fritt free from metal and in the other the mixture of ground fritt and metal. Over the mouth of the boxes fine cheese cloth was placed and bound on with rubber bands.

Two of the steel plates were now chosen and the lime scrubbed off with a steel brush. They were washed off with distilled water and wiped carefully with a clean moist sponge. This was done because it was desired to get the film of water of a uniform thickness as otherwise the enamel would crack and draw. Also too thick a film would cause too thick a layer of enamel to be put on at that place. This happens because the thickness of the enamel is determined to some extent by the evenness of color. If the film of water is thicker in some places than in others, a darker color will result and more enamel will be powdered on that spot than on the remainder of the plate. The numbers of the plates were now entered in the data book. The powdered enamel was carefully shaken on the plates to a thickness of approximately $3/32$ of an inch. The temperature as given by the pyrometer was now noted and recorded, the plates taken one at a time, put in the furnace end to end on the cupels, and the time recorded. The melting down of the enamel was watched through

a peep hole in the door and as soon as the enamel melted and flowed smoothly the plates were taken out and put on top of the furnace to be annealed slightly. Three plates of the same percent of metal were run and a plate of the unadulterated ground fritt was run as duplicate for each of them.

Before attempting to run any plates it was thought best to try a few plates both to test for the best temperature and also to gain some practice in enamelling. Four plates were taken and enameled and run at 1000°C., 960°C., 800°C., and 780°C. The plate no. 75 run at 1000°C. was transparent, glassy, had a yellowish brown color, was crazed badly and the temperature was so high that it drew the enamel away from the edges leaving the metal bare. Plate no. 85 run at 960°C. acted in much the same way. Plate No. 8 did not draw away from the edge and had fewer bubbles holes than the others run at higher temperatures. Plate No. 84 was run at 780°C. and did not differ materially from No. 8. From these plates it was decided to run the enamel at temperatures somewhere around 800°C.

The following tables show the data obtained in these experiments.

TABLE No. III.

No. plate	No. enamel	Percentage metal.	Time			Temperature.	
			B	E	D	B	E
119	91	-----	2:16	2:20	4	820°	810°
144	"	0.1 Aluminum	"	2:19	3	"	"
145	"	-----	2:24	2:27	3	830°	830°
143	"	0.1 Aluminum	"	2:26	2	"	"
00	"	-----	2:37	2:41	4	910°	820°
142	"	0.1 Aluminum	"	2:40	3	"	"
113	"	-----	2:56	3:00	4	820°	830°
120	"	0.5 Aluminum	"	2:59	3	"	"
153	"	-----	3:04	3:07	3	820°	930°
150	"	0.5 Aluminum	"	"	3	"	"
138	"	-----	2:13	2:17	4	840°	820°
106	"	0.5 Aluminum	"	"	4	"	"
139	"	-----	3:40	3:44	4	820°	840°
121	"	2.5 Aluminum	"	"	4	"	"
123	"	-----	3:45	3:48	3	840°	840°
133	"	2.5 Aluminum	"	"	3	"	"
147	"	9-----	3:49	3:52	3	845°	855°
137	"	2.5 Aluminum	"	"	3	"	"

REMARKS.

- No. 119:- Crazing, pin holes, bubbles.
 " 144:- Same as No. 119, more bubbles.
 " 145:- Crazing, bubbles, burned spots.
 " 143:- Larger bubbles than 145, no burned spots.
 " 00:- See No. 145.
 " 142:- See No. 144.
 " 113:- Same as No. 119.
 " 120:- Larger bubbles, less crazing than in No. 113.
 " 153:- Pin holes.
 " 150:- Same as No. 120.
 " 138:- Large shrinkage spots.
 " 106:- Same as 150, with shrinkage spots.
 " 139:- See No. 119.
 " 121:- Fluffed up with extreme bubble holes.
 " 123:- See No. 119.
 " 133:- " " 121.
 " 147:- " " 119.
 " 137:- " Nos. 121 and 133.

TABLE No. IV.

No. plate	No. enamel.	Percentage metal.	Time.			Temperature.	
			B	E	D	B	E
146	91	-----	2:39	2:44	5	820°	800°
103	"	0.1 Magnesium	"	2:43	4	820°	800°
154	"	-----	2:44	2:47	3	820°	800°
104	"	0.1 Magnesium	"	"	3	"	"
117	"	-----	2:49	2:53	4	840°	820°
114	"	0.1 Magnesium	"	2:52	3	"	"
107	"	-----	3:12	3:16	4	840°	800°
155	"	0.5 Magnesium	"	"	4	"	"
111	"	-----	3:17	3:20	3	840°	820°
163	"	0.5 Magnesium	"	"	3	"	"
130	"	-----	3:23	3:26	3	840°	820°
122	"	0.5 Magnesium	"	"	3	"	"

NOTE:- The 2.5 % magnesium fritt was not used as the 0.5% showed such large bubbles.

REMARKS.

No. 146:- See No. 119. Page 20.
 " 103:- Smaller pin holes, flowed well.
 " 154:- See No. 119, page 20.
 " 104:- Smaller pin holes, flowed well.
 " 117:- See No. 119, page 20.
 " 114:- Smaller pin holes, flowed well.
 " 107:- See No. 119, page 20.
 " 155:- No good, shrinkage from edges.
 " 111:- See No. 119, page 20.
 " 163:- Large bubble holes.
 " 130:- See No. 119, page 20.
 " 122:- Large bubble holes.
 "

TABLE No. V.

No plate.	No. enamel.	Percentage metal.	Time.			Temperature.	
			B	E	D	B	E
109	91	-----	4:36	4:39	3	840°	840°
129	"	0.1 Zinc	"	"	3	"	"
151	"	-----	4:39	4:42	3	840°	860°
161	"	0.1 Zinc	"	"	3	"	"
000	"	-----	4:44	4:47	3	860°	830°
140	"	0.1 Zinc	"	"	3	"	"
162	"	-----	3:00	3:03	3	860°	860°
124	"	0.5 Zinc	"	"	3	"	"
123	"	-----	2:58	3:01	3	860°	880°
131	"	0.5 Zinc	"	"	3	"	"
118	"	-----	3:05	3:08	3	860°	880°
110	"	0.5 Zinc	"	"	3	"	"
149	"	-----	3:20	3:22	2	920°	880°
156	"	2.5 Zinc	"	"	2	"	"
135	"	-----	3:23	3:26	3	880°	860°
108	"	2.5 Zinc	3:23	"	3	"	"
160	"	-----	3:27	3:30	3	840°	840°
112	"	2.5 Zinc	"	"	3	"	"

REMARKS.

No. 109:- See No. 119, page 20.
 " 129:- White, few large bubbles.
 " 151:- See No. 119, page 20.
 " 161:- White, large bubbles.
 " 000:- See No. 119, page 20.
 " 140:- White, fewer & larger bubbles.
 " 162:- See No. 119, page 20.
 " 124:- White, fewer bubbles, drew from edge.
 " 123:- See No. 119, page 20.
 " 131:- White, few bubbles.
 " 118:- See No. 119, page 20.
 " 110:- Like No. 131, crazed badly.
 " 149:- See No. 119, page 20.
 " 156:- Very large bubbles, drew from edges badly.
 " 135:- See No. 119, page 20.
 " 108:- " " 156. " 22.
 " 160:- " " 119, " 20.
 " 112:- " " 156, " 22.

TABLE No. VI.

No. plate.	No. enamel.	Percentage metal.	Time.			Temperature.	
			B	E	D	B	E
52	91	-----	4:54	4:57	3	840°	840°
8	"	0.1 Copper	"	"	3	"	"
157	"	-----	4:58	5:01	3	840°	850°
156	"	0.1 Copper	"	"	3	"	"
132	"	-----	5:02	5:04	2	840°	860°
166	"	0.1 Copper	"	"	3	"	"
127	"	-----	4:56	4:59	3	840°	820°
110	"	0.5 Copper	"	"	3	"	"
126	"	-----	4:40	4:43	3	840°	860°
125	"	0.5 Copper	"	"	3	"	"
116	"	-----	4:44	4:46	2	840°	860°
134	"	0.5 Copper	"	"	2	"	"
83	"	-----	5:02	5:05	3	840°	840°
79	"	2.5 Copper	"	"	3	"	"
58	"	-----	5:07	5:09	2	840°	860°
115	"	2.5 Copper	"	"	2	"	"
141	"	-----	5:10	5:13	3	880°	820°
47	"	2.5 Copper	"	"	3	"	"

REMARKS.

- No. 52:- See No. 119, page 20.
 " 8:- Very few bubbles, drew away from edge.
 " 157:- See No. 119, page 20.
 " 156:- " " 52 " 23.
 " 132:- " " 119, " 20.
 " 166:- Bubbles, see no. 52, page 23.
 " 127:- See No. 119, page 20.
 " 110:- White, not many bubbles, flowed from edge.
 " 126:- See No. 119, page 20.
 " 125:- " " 110, " 23, copper separated out.
 " 116:- " " 119, " 20.
 " 134:- White, full of bubble holes.
 " 83:- See No. 119, page 20.
 " 79:- Holes, green with copper.
 " 58:- See No. 119, page 20.
 " 115:- " " 83, " 23.
 " 141:- " " 119, " 20.
 " 47:- " " 83, " 23.

The enamels in Table No. II were run before the aluminum was washed with ether. The aluminum in this case caused more bubble and pin holes than when not used. However, these bubble holes were justly or unjustly blamed on the oil in the aluminum and so before any other enamels were run the metals were all washed in ether, as mentioned before. Trouble also occurred by poor enamelling, either the enamel was powdered on too thick or too thin and in most cases rather unevenly.

The next Table, No. III, shows the results of 0.1%, 0.5%, and 2.5% aluminum. The temperatures at which these plates were run was approximately 820° C. The table shows that the time for fusion was three to four minutes. In all of the plates the aluminum seemed to cause pin holes rather than prevent them as was expected. In the case of the 2.5% aluminum the enamel fluffed up like foam and formed holes as large as one-half inch in diameter with a sort of honey-combed structure.

The fourth Table is the results of the metal magnesium. The 0.1% magnesium enamel seemed to give fairly good results. The pin holes were less than in the pure enamel and the enamel seemed to flow better. The 0.5% magnesium caused such large bubbles that the 2.5% enamel was not tried.

Table No. V. gives the experiments with Zinc. In this case the zinc resulted in the for-

mation of a white enamel. The 0.1 % zinc formed fewer and larger bubbles. The results were the same with the 0.5% zinc except that it also drew away from the edge of the plate. The 2.5% zinc enamel formed very large holes and drew up in a sort of wad in the middle of the plate.

The results of the remaining metal copper is found in Table No. VI. The 0.1% copper enamel gave the best results. The copper seemed to lessen the number of bubbles but at the same time to cause the enamel to draw away from the edges of the plate. The 0.5% copper enamel was white and there were more bubble holes than in the pure enamel. The 2.5% enamel was full of holes and green with copper.

RESULTS.

These experiments have probably not been carried far enough to give very positive results and further research might establish different conclusions. However, the following conclusions may be drawn from the work described here.

(1)- A small percentage of magnesium and copper have a beneficial effect. It may be because of the reducing action of these metals or it may result from some other reason.

(2)- A larger percentage of these metals than 0.5 has a derogative influence. The data is not sufficient to attempt an explanation for this.