ORIGINAL PAPERS AND DISCUSSIONS

THE CAUSES AND CONTROL OF FISH SCALING OF ENAMELS FOR SHEET IRON AND STEEL¹

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ABSTRACT

Data obtained.—This paper presents measurements of the following factors and properties and their influences upon fish scaling in the case of typical single and three-coat enamels: time and temp. during melting of the frit; fusibility of the enamel; coeff. of expansion of the enamel, and of a variety of representative irons and steels up to 500°C (accuracy about 0.1%); annealing the enamel coat after firing; chem. comp. of the steels and irons; mechanical treatment (rolling, spinning, drawing, and so forth of the stock; microscopic surface structure of the stock; effect of chem. comp. upon thermal expansion of enamel.

Incidentally it was found that the formulas of Mayer and Havas for computing the thermal expansion of enamel from its chem. comp. can not be relied upon.

Conclusions.—On the basis of these exhaustive tests, the following conclusions have been drawn as to the causes and the control of fish scaling.

(A) **Causes.**—1. The cause of fish scaling lies in the difference of the coefficients of expansion of the enamel and the stock, that for steel being higher than for enamels so that the latter are under a compressive stress. The factors influencing this phenomenon are as follows: (a) Composition of the enamel as affecting the coefficient of expansion of the enamel; (b) Overfiring—thus volatilizing those substances which tend to keep the coefficient high; (c) Lack of annealing enameled ware, the enamel coating of which is a *glass* and should logically be treated as such.

2. Fish scaling is due secondarily to a number of factors which may affect the strength of the enamel or its adherence to the metal. (a) The physical condition of the surface of the metal as influenced by drawing, spinning, cold rolling or other mechanical treatment; (b) Composition of the glass as affecting its elastic strength; (c) Underfiring, enamel not fused to metals; (d) Cleanliness of the surface as regards removal of drawing compounds, grease, etc.

¹ Received June 13, 1921. Published by permission of the Director, Bureau of Standards.

(B) **Remedies.**—1. (a) Adjusting the composition of the enamel so as to increase its coefficient, *e. g.*, by decreasing the boric acid content; (b) Correct firing of the enamel to avoid unnecessary volatilization of such fluxes as soda and cryolite; 2. (a) Adjusting enamel composition to increase its strength; (b) Correct firing to give proper adherence. 3. Treatment of metal to give best adhesion by (a) cold rolling or other suitable mechanical treatment of the untreated steel; (b) thorough cleaning.

(C) **Summary.**—Broadly stated, then, fish scaling can be absolutely controlled by one or all of the following methods: (1) By the development of an enamel with an expansion fitting the metal; (2) by annealing the enameled ware; (3) by treatment of the metal as cold rolling or some other method of working; (4) by developing an enamel with a wide range of compressional elasticity and applying this enamel to metal treated as indicated above.

The subject of fish scaling of enamels has been much discussed among enamellers but comparatively little systematic investigation has been carried out in spite of the enormous losses occasioned in the industry by this defect, the only work recorded being that of Shaw.¹ Fish scaling may be defined as the spontaneous chipping or scaling of small particles of enamel from an enamel surface. These scales may vary from $1/64$ to $3/8$ of an inch in diameter and appear to be confined to the enamel surface although on close examination they are usually found to extend down to the steel, the extent of fracture depending on the type and size. The smaller scales are usually very numerous while the larger type are generally few in number.

The Enameled Metals Section of the Bureau of Standards has been conducting during the past year and a half an extended investigation of this subject, and preliminary reports were presented at the annual meeting of the American Ceramic Society in February, 1920, and also at a joint conference of the Enamel Division of the Society and the Sheet Metal Ware Manufacturers Association at this Bureau, June 15, 1920. In attacking this problem, the initial work was done on gray ware enamels since these are the least complex in composition and in method of application. As a basis for the compounding of the enamels, an average of several commercial formulas, having the following composition, was selected:

¹ J. B. Shaw, "Fish Scaling," *THIS JOURNAL*, 3, 489-98 (1920).

	Raw batch per cent	Raw batch for 100 lbs. melted	Melted per cent	
Feldspar.....	49.0	62.5	62.5	
Borax.....	35.0	45.0	{ 16.3 B ₂ O ₃ 7.45 Na ₂ O }	
Soda ash.....	7.8	10.0	5.8 Na ₂ O }	14.7
Soda nitre.....	3.1	4.0	1.45 Na ₂ O }	
Bone ash.....	3.5	4.5	4.5	
Antimony oxide.....	1.6	2.0	2.0	
	100.0	128.0	100.0	
Empirical formula	0.285 K ₂ O } 0.600 Na ₂ O } 0.115 CaO }	0.285 Al ₂ O ₃ } 0.600 B ₂ O ₃ } 0.018 Sb ₂ O ₃ }	1.72 SiO ₂ 0.076 (PO ₄) ₂	

The composition of the frit is based on the assumption that such materials as feldspar, bone ash, antimony oxide, and cryolite lose no weight during melting. The method of calculation is similar to that described by Staley in his treatise on enamels for cast iron.¹

The results of preliminary experiments and the desire to bring out clearly the effect of feldspar on fish scaling showed the advisability of working with three groups of enamels, so arranged that the feldspar remained constant in any group, the variations being made in the fluxes. The feldspar content was set at 59 per cent, 62.5 per cent, and 66 per cent, respectively, the preliminary experiments having demonstrated that these about covered the field of workable enamels. The groups shown in tables 1 and 2 have served as the basis for the work on the gray ware enamels.

TABLE 1—COMPOSITION OF MELTED ENAMELS

Material	Constant parts		
	59% feldspar group	62.5% feldspar group	66% feldspar group
Feldspar.....	59.0	62.5	66.0
Sodium oxide.....	10.0	10.0	10.0
Boric oxide.....	14.0	14.0	10.5
Fluorspar.....	3.5	0.0	0.0
Bone ash.....	4.5	4.5	4.5
Antimony oxide.....	2.0	2.0	2.0
Variable.....	7.0	7.0	7.0
Totals.....	100.0	100.0	100.0

¹ H. F. Staley, "Manufacture of Cast Iron Enameled Ware," *B. S. Tech. Paper*, No. 142 (1919).

Material	Amount	Enamel	Variable parts, Enamel	Enamel
Sodium oxide.....	7	A-20	A-1	A-16
Boric oxide.....	7	21	2	12
Fluorspar.....	7	22	3	17
Cryolite.....	7	23	4	18
{ Sodium oxide..... }	3.5	24	6	9
{ Boric oxide..... }	3.5			
{ Sodium oxide..... }	3.5	25	7	19
{ Fluorspar..... }	3.5			
{ Boric oxide..... }	3.5	26	10	14
{ Fluorspar..... }	3.5			
Additions for direct increases of feldspar		21a—Enamel 21 plus 5% feldspar		
		21b—Enamel 21 plus 10% feldspar		
		23a—Enamel 23 plus 5% feldspar		
		23b—Enamel 23 plus 10% feldspar		

TABLE 2—BATCH COMPOSITION OF ENAMELS—WEIGHTS OF RAW MATERIALS TO GIVE 100 PARTS MELTED

Material group		Constant parts		
		59% feldspar group	62.5% feldspar group	66% feldspar group
Feldspar.....		59.0	62.5	66.0
Sodium nitrate.....		4.0	4.0	4.0
Soda ash.....		4.0	4.0	6.7
Borax.....		38.2	28.2	28.7
Fluorspar.....		3.5	0.0	0.0
Bone ash.....		4.5	4.5	4.5
Antimony oxide.....		2.0	2.0	2.0
Material	Amount	Enamel	Variable parts, enamel	Enamel
Soda ash.....	12	A-20	A-1	A-16
Boric acid.....	12.4	21	2	12
Fluorspar.....	7	22	3	17
Cryolite.....	7	23	4	18
{ Soda ash..... }	6.0	24	6	9
{ Boric acid..... }	6.2			
{ Soda ash..... }	6.0	25	7	19
{ Fluorspar..... }	3.5			
{ Boric acid..... }	6.2	26	10	14
{ Fluorspar..... }	3.5			
Additions for direct increase in feldspar		21a—Enamel 21 plus 5 parts feldspar		
		21b—Enamel 21 plus 10 parts feldspar		
		23a—Enamel 23 plus 5 parts feldspar		
		23b—Enamel 23 plus 10 parts feldspar		

The various enamels were compounded by weighing up the base enamel in each group and adding to it the required amount of flux to produce the desired composition. For example, A-20 was made by weighing the raw materials listed in the 59% feldspar group (table 2), and adding to it 12 parts of soda ash. A-2 was compounded by weighing the base for the 62.5% feldspar group and adding to it 12.4 parts of boric acid. The complete batches were then mixed for melting.

For preliminary tests, the enamels were weighed in 4.5 lb. batches, mixed thoroughly by hand and by sieving. These were then melted in fire-clay crucibles in a pot furnace. An attempt was made to keep a uniform melting temperature, a number of readings with an optical pyrometer indicating a temperature of about 1170°C (2140°F).

The average time of melting was about one hour, the operation being carried to a point where the melt was as free from bubbles as possible under the conditions of crucible melting. The melts were quenched in water, dried and then ground wet in porcelain ball mills, the following mill batches being used:

Frit.....	1000 grams
Clay.....	60 "
Magnesium carbonate.....	5 "
Water.....	55 ccm.

The batches were ground for seven hours which was sufficient to permit them to pass an 80 mesh sieve.

The enamels were then applied to 2 × 3 inch plates of a 20-gauge iron, hereafter designated as Iron A (see table 4). These had been prepared by boiling in a solution of caustic soda for about 20 minutes to remove oil, then rinsed in clear water and pickled in a hydrochloric acid bath of one part acid (1.18 sp. gr. 36% HCl), to seven parts water. This gave an acid content of about 5.5 per cent.

After pickling, the plates were rinsed several times in water and were then kept under water until ready for the application of the enamels. The latter were applied by dipping, epsom salts being used as the flotation medium. The plates were then dried and were ready for firing.

A definite firing schedule was established to determine the effect of variations in firing, so that there might be a basis of comparison for various enamels under the same heat treatment. The following schedule was made broad enough to cover the range of the various enamels:

Temperature in degrees		Time		
C	F	in minutes		
760	1400	2	4	6
820	1508	1 ¹ / ₂	3	4 ¹ / ₂
880	1616	1 ¹ / ₄	2 ¹ / ₂	3 ³ / ₄
940	1724	1	1 ¹ / ₂	2

Ten samples of every enamel were made for each temperature and firing period. The plates were fired in a Hoskins electric muffle furnace and were supported on a grid of wrought iron which was left in the muffle continuously in order to keep it at furnace temperature. A platinum-platinum-rhodium thermocouple enclosed in a very thin porcelain tube was placed directly over the plates and, the muffle being about $6 \times 8 \times 12$ inches, the temperature could be regulated fairly accurately within 10°C of the accepted standard.

Effects of Variations in Composition and in Firing

The following conclusions can be drawn from this phase of the work:

(1) In a normal enamel fish scaling increased with increase in temperature or length of time of firing beyond normal firing conditions.

(2) Too low a temperature or too short a firing period produced blistering and bubbling, while high temperatures and long periods resulted in burning off of the enamel.

(3) Considering only those results in which the enamels were properly fired, the following order gives the relative effects of various fluxes in reducing fish scaling, the most effective being placed first:

- a. Cryolite
- b. Fluorspar
- c. Sodium oxide
- d. Boric oxide

(4) The burning range of the enamels is lengthened by the

following materials in the order named, the most effective being noted first:

- a. Cryolite
- b. Fluorspar
- c. Boric oxide
- d. Sodium oxide

Fusion Tests of Enamel

On the basis of the above results, it was assumed that this "fish scaling order" of the fluxes followed the relative fusibilities of the enamels, but further work has proven otherwise. Fusion tests of cones prepared from these enamels have placed the fluxing action of the materials in the following order, the first named giving the most fusible enamels:

- a. Cryolite
- b. Sodium oxide
- c. Fluorspar
- d. Boric oxide

These determinations were checked by melting small layers of

FIG. 1.—Relative fusibilities of gray ware enamels.

enamels on ground coated plates at various temperatures for periods of two minutes and noting the temperature at which the enamels fused. These temperatures, while not agreeing with the softening points of the cones, place the fluxes in the same relative position as shown in the curves, figure 1.

Effect of Variations in Smelting Procedure

To determine the effect of over- and under-smelting, the first four enamels, A-1, A-2, A-3, and A-4, of the group containing 62.5 per cent feldspar were selected. Three batches of each enamel were made and melted as described previously but with the following changes in the duration of melting. The under-melted batch was carried to the point where all the raw materials were apparently melted, no attempt being made to drive off the gases. This required on an average about 40 minutes. The medium melted enamels were melted until the gases had been driven off and the melt had become quiescent. This required on an average about 55 minutes. The over-melted enamels were held at this same point for about 15 minutes longer, giving on an average about 70 minutes. These enamels were prepared and applied, as described previously in this paper, to 2×3 inch plates of Iron A and a steel designated as Steel B.

The following conclusion may be drawn as to the effect of various treatments in melting:

(1) Increasing the time of melting of an enamel has apparently but slight effect on the tendency to fish scale. It must be remembered, however, that while the melts were apparently over-melted in 70 minutes, the increased effect of melting is probably not as great as that encountered in actual practice where the results tend to show that over-melting increases fish scaling, undoubtedly due to the volatilization of fluxes like sodium oxide¹ which tend to decrease fish scaling.

The effect on fish scaling of variation in the steel is very apparent in this part of the investigation since the scales on Steel B are much larger than those on Iron A.

¹ Poste and Rice, "Effect of the Degree of Smelting," *THIS JOURNAL*, 1, 221-37 (1918).

A number of these gray ware enamels typical of those prone to fish scale and others free from this defect have been applied to the various steels and irons listed in tables 4, 5, 6, and 7. The general results confirm those obtained with Iron A and Steel B although there is a tendency on the part of certain stocks to develop a greater or less tendency to fish scale even when coated with the same enamels. Steels C and D, for instance, which are cold rolled strip steel, although not considered as enameling stock, show a complete freedom from the defect. It is evident therefore that further consideration must be given to the various properties of the stocks such as expansivity, chemical composition, mechanical condition, and so forth. These have been carefully studied with the results shown in the following sections.

Thermal Expansion of Enamels

The foregoing studies have indicated that composition and heat treatment of the enamel have a marked effect on fish scaling. There are variations in some of the results which undoubtedly are consequences of improper manipulation. There still remains, however, the fundamental problem of why enamels fish scale and an explanation for the variations in results obtained with various steels and irons.

Because of the nature of the defect, the most logical place to look for the solution is in the relative thermal expansivities of the enamels and stock. Tabulated values of coefficients of expansion for iron and steel usually indicate a value of 12×10^{-6} to 13×10^{-6} per °C. Empirical formulas for the enamel values in terms of composition have been supplied by Winkelman and Schott and by Mayer and Havas.¹ By using these formulas it has long been considered possible to mix an enamel which will match the stock. We are all familiar with the attempts and failures of this method. A further confusion has arisen due to the fact that different specimens of stock of practically the same expansive qualities have shown different results. With these contradictions and indefinitenesses hindering further progress, it was decided to make a comprehensive survey of the subject of

¹ Mayer and Havas, "Coefficient of Expansion of Enamels and Their Composition," *Speersaal*, **44**, 188 (1911).

expansion, disregarding for the time being all previous work on this phase by other investigators.

In this work the regular equipment of the Expansivity Section of the Bureau was utilized, the accuracy of which may be stated as 0.1 per cent.

For the study of the metal stocks a number of representative irons and steels were selected and strips were cut from the plates approximately one inch wide and 14 inches long. In commencing the work on enamels, specimens were prepared from both the molten frit and the enamel prepared for dipping, but no difference was observed so the work was continued on the latter alone.

The specimen rods of enamel were 14 inches long and triangular in cross section, being about $\frac{3}{8}$ inch along a side. These were prepared by drying the enamel slip, placing the resulting powder in sheet iron troughs lined with asbestos paper and melting the powder to an enamel rod in the enameling furnaces at approximately enameling temperatures. This required about five minutes, after which the troughs and contents were removed to an enameling furnace at 500°C (932°F) and cooled slowly to room temperatures.

In the expansivity furnace, the specimens were supported horizontally in quartz tubes. V-shaped rings were cut around the specimens near each end so that 2-mil annealed platinum wires could be fastened in these. Each wire, hanging through a hollow tube below the end of the specimen and extending downward through and below the furnace, had at its lower end a vane (or weight) immersed in oil in order to dampen the vibrations. Heating was effected by electric resistance coils (outside, inside, and end coils). With careful manipulation it was possible to adjust the circuits so that during an observation the specimen was at a uniform temperature within 0.1°C, from end to end.

The length changes were determined with a comparator consisting of two microscopes rigidly clamped on an invar bar at a distance from each other equal to the distance between the grooves of the specimen (30 cm.). The microscopes were so arranged that they could first be sighted on a standard-length bar kept at constant temperature, and then on the vertically suspended wires which were in the grooves at the ends of the specimen.

FIG. 2.—Expansivity apparatus.

The apparatus shown in figure 2 was used for this research. This figure portrays the essential method of making observations on materials. The furnace is shown with the top lifted. The traveling microscopes, which are sighted (simultaneously) on the two vertical wires hung from the specimen, are displaced to the right in order to show the construction of the tube protecting the vertical or drop wires. The left oil pot is removed to show the weight attached to the wire.

The temperatures in the furnace were determined by means of a platinum platinum-rhodium thermocouple. It had been noted that enamels became viscous on enameled plates at about 550°C (1020°F) so it was decided to make the expansion studies between room temperatures and 500°C .

TABLE 3—COEFFICIENTS OF EXPANSION $\times 10^6$

Enamel	GRAY WARE ENAMELS AND STEELS					
	1. Room to 200°C	2. Room to 400°C	3. Room to 500°C	4	5	6
A-1.....	10.9	11.3	13.9	11.7	0.8	0.4
A-2.....	8.8	9.4	10.7	9.4	.6	.0
A-3.....	9.4	10.7	13.2	9.9	1.2	.8
A-4.....	9.8	11.6	13.4	11.0	1.2	.6
A-12.....	8.2	9.3	10.6	9.7	1.5	.4
A-16.....	9.4	10.1	10.8	12.0	2.6	1.9
A-17.....	9.1	10.2	11.9	10.2	1.1	.0
A-18.....	9.3	10.4	12.6	11.3	2.0	.9
A-20.....	10.1	10.9	13.8	11.6	1.5	.7
A-21.....	8.1	10.1	11.3	9.3	1.2	.8
A-21a.....	8.1	9.0	10.2	9.2	1.1	.2
A-21b.....	8.3	9.1	10.5	9.2	.9	.1
A-22.....	9.5	10.6	13.7	9.8	.3	.8
A-23.....	10.0	11.4	13.8	11.0	1.0	.4
A-23a.....	8.8	10.4	11.8	10.9	1.1	.5
A-23b.....	9.3	10.6	13.5	10.7	2.0	.1
Steel A-A.....	12.7	14.1	14.6			
Steel A-B.....	12.7	14.1	14.5			
Steel A-D.....	13.1	14.2	14.6			
Steel C-hd.....	12.6	14.2	14.5			
Steel C-an.....	12.9	14.1	14.8			
Steel C-an-el 25%....	12.7	13.8	14.2			
Steel B.....	12.8	14.0	14.4			
Iron A.....	13.0	13.9	14.4			
Iron A-el 20%.....	12.7	14.0	14.6			

(1, 2, 3) Observed values for coefficients of expansion of enamels and steel from cooling curves.

(4) Calculated values of coefficients of expansion from Havas and Mayer's values.

(5) Calculated values compared with Bureau observation—room to 200° C, differences.

(6) Calculated values compared with Bureau observation—room to 400° C, differences.

The values for the various steels and enamels studied are given in table 3, as well as the figures computed from the values given by Havas and Mayer¹ for various oxides. In figures 3, 4, and 5 are shown the curves for the various enamels as compared with steel.

In these curves the temperatures are plotted as abscissas and the expansions per unit length as ordinates. The expansion

FIG. 3.—Expansion of enamels A-20 to 23 and stock matched at 500°C.

¹ *Loc. cit.*

for the stock was plotted first, and, for the reasons stated above, the enamel expansions plotted to agree with the stock at 500°C. The actual total expansion of stock per unit length, from room to any higher temperature, may be read directly at the left of the curve. In getting the actual expansions of the enamels between any two temperatures it will obviously be necessary to take the difference of the two readings at the left corresponding to the respective values of the temperature interval.

FIG. 4.—Expansion of enamels A-1 to 4 and stock.

A brief discussion of the above is appropriate at this time. Heat and mechanical treatments failed to modify the expansivities of these stock steels and irons, which is contrary to the results in cast iron enameling where growth of the iron casting is encountered as a result of heating. The values of the coefficients of expansion of the various stocks in table 3 will be found so nearly the same that an extended discussion is not necessary at this

FIG. 5.—Expansion of enamels A-12 to 18 and stock.

time. The letters (*hd*) after specimen C refer to hard cold rolled material. Similarly (*an*) indicates annealed and (*el*) indicates elongated or stretched in the tensile apparatus.

From a study of these values it is evident that cold rolling, annealing, stretching, and so forth, have only a negligible effect, if any at all, on the expansivities of stock. Furthermore, the general character of the heating and cooling curves obtained in these tests show that no permanent changes were introduced in the material (so far as expansivity is concerned) since they all returned to their original lengths after testing.

The enamel expansions are lower than those for steel although both increase with temperature; the former, however, increasing faster than the latter. As has been stated previously, the enamels become viscous above 500 or 550°C. At these temperatures we assume that they adapt themselves perfectly to all changes in the stock. Upon cooling there is some temperature at which the enamel becomes rigid and offers resistance to inequalities in contraction. This point has been selected as 500°C, although there is no objection to changing it to a few degrees higher or lower if desired. Accordingly all curves have been set to match at 500°C at which temperature there is an absence of all strains. The deviations of these curves at lower temperatures indicate the corresponding strains to be expected. In most instances the enamels have contracted faster on initial cooling (Enamels 1, 3, 4, 17, 18, 20, 22, 23) and are tending to compress the stock; however, before reaching room temperatures the enamels have slowed up and at normal temperatures all are being compressed by the stock.

Perhaps a more logical method will be to consider the ordinates of the curves referred to contractions rather than expansion. The dotted horizontal lines are arranged to indicate contraction on cooling from the solidification temperature. In figures 3, 4, and 5, this temperature has been taken as 500°C, in the remainder as 450°C. The values at the right of these curves refer to the actual contractions of all specimens on cooling below the fiducial temperature. For example, in figure 3, the contractions on cooling from 500°C to 100°C are as follows: A-21 contracted 0.0048 of

the length at 500°C and the stock contracted 0.0059 of the length at 500°C. The difference between the two contractions gives the expected strain at 100°C, *i. e.*, 0.0011. These values may be used in any system of units, *e. g.*, a 1 meter specimen of A-21 at 500°C if free to contract will have a length of 0.9952 meter at 100°C; or a one inch specimen will have a length of 0.9952 inch, and so forth. In practice we may expect a compromise and in reality that the enamel will be compressed below the 0.9952 value due to the greater tendency for contraction of the iron (to a length of 0.9941). Similarly the iron may never reach this lower value but may stop at a higher value due to the restraining effect of the enamel. Table 3 gives the complete assemblage of all values from the series A enamels and various steels and irons. All values in table 3 are expressed as millionths per unit length, per degree C.

Manifestly those enamels most widely separated from the stock at room temperature, A-12, A-21, should have the greater tendency to scale and those more nearly agreeing with stock at this temperature (A-1, A-4, A-20 and A-23) should exhibit a lesser tendency. These conclusions are borne out by the enameled specimens. It should be pointed out that while no enamel matches the stock absolutely, enamels do adhere satisfactorily and that this adhesion is due to the strength and elasticity of the enamel, and to the union of enamel and stock (either chemical or mechanical) and that by properly treating the stock by mechanical means (as will be shown later) it is possible to cause practically any enamel to adhere to any stock, regardless of the inherent strains set up. Unless these strains are later released by annealing as will be explained, the ware should not be expected to stand up under severe treatment.

As previously stated, the empirical formulas of Mayer and Havas are supposed to indicate the expansion of the various batches on the basis of chemical composition. While it is understood that the rate of expansion increases rapidly with temperature (see figures 3, 4, and 5) and that these values do not give complete information, still it was thought desirable to attempt to arrange their values to indicate, if possible, correct expansion at

some one temperature. By comparing the average values for twelve different enamels, it appears that the Mayer and Havas results most nearly indicate expansions for the range from room temperature to 400°C. The original articles, however, show that the values are taken from determinations over the range, room to 100°C. For comparison only, they are arranged near our column, room to 400°C. In some instances the empirical values run above and in other below the experimental. The extreme variation of these is greater than the widest variation for all twelve enamels. It so happens for this set of enamels (excluding the specials 21a, 21b, 23a, 23b) that, if we should state that all enamels will have expansions exactly equal to 10.6×10^{-6} (regardless of composition or otherwise) over the range, room temperature to 400°C, then the variations or errors would be less than those obtained by using Mayer and Havas values. A further question is raised as to the wisdom of ever using these values, as is shown by the expansion values observed for enamels 21, 21a, 21b, and 23, 23a, 23b. The addition of 5% feldspar to A-21 and 23 gives the 21a and 23a batch and the addition of 5% more, the 21b and 23b batch. The feldspar linear coefficient is 8.3×10^{-6} whereas the A-21 enamel computes 9.3×10^{-6} and the A-23 is 11.0×10^{-6} . In each case the addition of 5% feldspar might be expected, according to Havas, to reduce the coefficient and further, the latter enamel (23) should reduce more than the former (21) since its expansion computes 11.0×10^{-6} against 9.3×10^{-6} . Observation will show the values reduced, but in reverse order; number 21 from 10.1 to 9.0 = 1.1 and number 23 from 11.4 to 10.4 = 1.0. The addition of the next 5% feldspar might be expected to give similar (perhaps slightly less) reductions in coefficients; unfortunately it does not, but produces a definite increase in each case. This reduction and later increase may perhaps be explained on some such basis as follows: feldspar may tend to reduce all coefficients toward a value of 8.3×10^{-6} when mixed in batches of material wherein there is an excess of certain other constituent, but when the excess of this certain other constituent is overbalanced by an excess of feldspar the reverse is true. The authors are conscious of the fact that values over a range, room to 100°C, have been applied for a range,

room to 400°C. The range, room to 100°, would have indicated far greater variations and as stated before, the application was made at the point of greatest advantage for the Mayer and Havas values. A further defect in these tables is the fact that they give only a single value for the coefficient whereas the values for all the above specimens increase with increasing temperature. In a later paper, this phase will be treated more fully and an additional reason given, showing why it is impossible to secure relative values from these empirical tables.

We are forced to conclude that there is very little significance to be attached to these formulas of Mayer and Havas and that although they may appear to give results in some cases, there is always the uncertainty of knowing which cases are typical and which are exceptional.

The following conclusions may be drawn from this work:

(1) The coefficients of expansion and contraction are very nearly the same within the temperatures given for the various irons and steels used in this work. Therefore, the variations in fish scaling as evidenced in various steels can not be due to variations in the expansion and contraction of the various steels.

(2) Expansion of steel is greater than that of enamels by 3 to 40 per cent.

(3) The various constituents of the enamel have varying effects on the coefficient of expansion of the enamel.

(4) The values for the coefficients of the enamels between room temperatures and 200°C run from 20 to 40 per cent lower than those for steel.

(5) The coefficient of the enamels increases very rapidly above 200°C.

(6) The coefficient values computed from the Mayer and Havas' table are not accurate. Further, this method gives only a single value whereas it is evident that the coefficient is not constant for the various temperatures.

(7) If held at a constant temperature, between 200 and 300°C the enamels show shrinkage.

Effect of Annealing Enamels

Assuming then that fish scaling is due to the difference in the contractions of the steel and enamel and also bearing in mind further that enamels show shrinkage on slow cooling, annealing or slower cooling of the enameled ware should decrease or even eliminate fish scaling.

A study was made on small plates and stamped bowls coated with enamels A-21 and 23, half of the pieces being cooled normally and the other half placed in an annealing furnace at 500 °C and allowed to cool slowly in approximately four hours to room temperature. It was assumed that this method would allow the enamel to shrink and more nearly match the steel coefficient. A further advantage would be that it would allow the steel to cool and contract at the same time that the enamel contracts, whereas, if allowed to cool suddenly, the protected steel will be hotter than the exposed enamel, and after the enamel becomes rigid will have a longer range of temperature to travel with a larger coefficient, thus intensifying the strain between enamel and steel.

It was clearly demonstrated that annealing of the enameled ware eliminated fish scaling and that the normal air-cooled ware did fish scale, especially with the high boric oxide enamel A-21, which has a low coefficient. The annealed ware has been examined some eight months following the test and there are no indications of scale while the normal pieces scaled within 24 hours following firing.

This study is of value from two viewpoints. First, it demonstrates clearly the value of the coefficient of contraction theory, and secondly, while annealing may be objected to commercially because of the extra cost it entails under present conditions, it points to a decided advantage in the use of continuous enameling furnaces of a tunnel type where provision will undoubtedly be made for cooling the ware slowly as it emerges from the firing zone.

Chemical Compositions of Steels and Irons

When it was shown by thermal expansion studies of the steel and iron stock that many variations in their enameling properties could not be laid to variations in the coefficients of expansion,

it was deemed advisable to make a study of the chemical constituents most likely to affect the enameling qualities. The compositions of the various stocks were as follows:

TABLE 4—ANALYSES OF VARIOUS ENAMELING STOCKS

Stock	C	Results of analyses in per cent					Results in enameling
		Mn	P	Si	S	Cu	
Steel C*...	0.08	0.37	0.020	0.001	0.070	0.022	No fish scaling
Steel D**...	0.066	0.34	0.011	0.002	0.052	0.033	No fish scaling
Iron A.....	0.014	0.009	0.006	0.005	0.025	0.056	Some scaling
Steel E....	0.060	0.36	0.020	0.030	0.056	0.082	Considerable scaling
Steel B....	0.055	0.33	0.008	0.002	0.026	0.270	Badly scaled

* C, hard cold rolled strip steel

** D, dead soft cold rolled strip steel

A review of these analyses and enameling results seemed to bring out very decidedly the fact that fish scaling was intimately related to the copper content of the steel or iron used as the base for the enamel. However, these stocks were comparatively low in copper with the exception of Steel B and it was, therefore, decided to experiment on other enameling steels which would be typical of those containing higher contents of copper. The tests were, therefore, continued on enameling steels of the following composition:

TABLE 5—ANALYSES OF STEELS

Stock	Gauge	Results of analyses in per cent					Results in enameling
		C	Mn	P	Si	S	
A-A Open hearth....	20	0.075	0.41	0.015	0.010	0.040	0.132 Good
A-B Open hearth....	16	0.075	0.40	0.014	0.010	0.039	0.136 Poor
A-C Open hearth....	24	0.065	0.37	0.035	0.010	0.042	0.148 Fair
A-D Open hearth....	20	0.120	0.34	0.075	0.010	0.041	0.192 Bad
A-E Bessemer.....	20	0.090	0.35	0.080	0.009	0.028	0.160 Fair

These steels were enameled, in the regular method outlined, with Enamels A-21 and 23. It was soon noted that while the gauge has some effect on fish scaling, the heavier gauge steel apparently showing most scale, there was no definite increase of scale with increase in the copper content of the steels. The series was hardly systematic enough, however, to give conclusive proof so an attempt was made to procure a series of steels and irons with increasing copper content from small to large amounts. This resulted in a study on the stock of the following chemical composition:

TABLE 6—ANALYSES OF IRON SHEETS—COPPER SERIES

No.	S	P	C	Mn	Cu	Enameling results
2651	0.017	0.005	0.010	0.012	0.018	Many scales
2636	0.026	0.006	0.014	0.015	0.060	Very few fine scales
2641	0.025	0.008	0.012	0.018	0.090	Few fine scales
2637	0.025	0.006	0.012	0.018	0.190	Few scales
2640	0.024	0.010	0.010	0.018	0.263	Many scales

TABLE 7—ANALYSES OF STEEL SHEETS—COPPER SERIES

No.	S	P	C	Mn	Cu	Enameling results
2638	0.029	0.008	0.11	0.410	0.072	Large number of fine scales
2642	0.020	0.011	0.08	0.358	0.094	Large number of fine scales
2643	0.030	0.010	0.11	0.408	0.136	Many large scales
2639	0.020	0.010	0.09	0.388	0.316	Many large scales

It was soon made apparent that fish scaling was not directly related to copper content and that the results of the systematic study did not bear out the earlier conclusions drawn in this connection for there was still evident widely differing results in the amount of fish scaling on the various steels.

It is sufficient to state that variations in enameling results as regards fish scaling do not appear to be due to the chemical composition of the stock within the ranges studied (and these steels and irons all fall within the limits prescribed for enameling stocks) but rather to their mechanical treatment as will be shown later in this work.

Mechanical Treatment of Enameling Stock

While the foregoing results show that fish scaling may be prevented by selecting an enamel of proper expansivity, at the same time they indicate that other factors have effects which can not be ignored. For example, Enamel A-21 adheres to Steel C but does not adhere to Iron A nor A-B and D Steels. Enamel A-23 gives very little scaling with any of the stocks; one reason, at least, being the nearer match in expansion of Enamel A-23. Now considering expansivity only we should conclude that if Enamel A-21 will adhere to Steel C then it should likewise adhere to Iron A which has practically the same expansivity as Steel C.

The other factors which must be considered to account for the numerous failures of Enamel A-21 are lack of ability to stand up under compressive stress or poor union of enamel and stock.

In many instances, the failure appears to be due to the brittleness or weakness under compressive stress. The form of the scale itself being of varying thickness from full depth at one part to a sharp edge at the outer part at once suggests a compressional failure. It might appear that the roughness or porosity of the stock was sufficient to allow the enamel to penetrate and interlock (figure 6) and that the scale snapped off the stock from a very small smooth area only (figure 7), but spread as it approached the outer enamel surface, giving the scale a form not greatly dissimilar to those of compressive failure specimens.

FIGS. 6 and 7 from adjacent sections. Same edge of enamel showing in both views.

FIG. 6.—Cross section of fish scale, $\times 215$. Where enamel adhered.

FIG. 7.—Cross section of fish scale, $\times 215$. Where enamel scaled.

FIG. 8.—Cross section of enamel, $\times 215$. Steel etched away.

FIG. 9.—Cold rolled steel and enamel, $\times 215$.

When larger areas of enamels chip away from the steel, immediately on cooling of the fired ware, failure is undoubtedly due to the lack of union between iron and enamel, and the phenomenon is to be differentiated from fish scaling. Failures of this type have been traced to imperfections in cleaning, pickling, coating of the stock, or similar defects.

All enamellers are familiar with the effects of shapes or patterns in vessels and have also noticed that the sides of a spun vessel do not scale as readily as the untreated bottom surfaces. Tests were made to determine what effects could be attributed to a possible difference in the rate of cooling of protected, and unprotected flat and curved surfaces, by carefully annealing the pans and then enameling. Apparently annealing of the stock had no effect on the fish scaling.

This process of elimination practically forces the theory of mechanical adhesion upon us as the determining factor in this special case. To verify the theory that greater working of the metal was responsible for lack of fish scaling on the sides of drawn and spun vessels, several strips of steel and iron were stretched to 10 per cent elongation. The strips were so clamped that only half of the strip was stressed, so that the comparative effects on fish scaling could be determined under exactly the same conditions.

The plates were cleaned and pickled in the regular way and Enamel A-21 was applied, the latter being typical of an enamel prone to fish scale. It was found in every case that the stressed portion was absolutely free of scale while the normal portion fish scaled, the line of demarcation between the two portions being very sharp in this respect. This effect is unquestionably due to the mechanical treatment of the iron. Expansion tests of both stretched and cold rolled specimens of steel and iron are recorded in table 3 (see Steel C, elongated, Iron A, elongated, and Steel C, hard), from which we see that this treatment has not changed the rate of expansion appreciably.

In casting about for some true explanation of this variation in properties of the steels, use was made of the microscope in studying the surfaces of the metal since it was believed that the

cause for variations would lie in the variations of surfaces. It was noted in these latter studies that the surfaces of Steels C and D (which steels had never developed scaling) were very smooth and regular in structure. It was presumed that the fact that these steels were cold rolled had possibly some effect on their enameling properties and samples of the various steels were given a cold rolling that decreased their thickness by about 0.015 of an inch, and at the same time polished the surface. These steel specimens when enameled gave perfect results and no fish scaling developed.

The results with cold rolling of iron were, however, not as promising. Although the development of scale was materially decreased on the treated iron, there was not the complete elimination of scale which it had hoped would result. It is evident that there is some difference in the effect of cold rolling on steels and on irons which must be explained.

It might be assumed that cold rolling had carried the metal beyond its elastic limits and had introduced certain permanent molecular changes in the metal beneficial from an enameling standpoint. That this is unlikely is shown by the fact that the same results were obtained in enameling regardless of whether the plates had been annealed or simply cleaned in a caustic solution following cold rolling and previous to pickling for enameling purposes.

Further, cold rolled specimens tested in the expansivity furnaces and therefore heated over a period of about 20 hours up to 625°C, at which temperature they were held constant for about two hours and then cooled slowly to room temperatures, behaved exactly as the normal rolled stock.

In mechanically treating the metal, either changes are produced in the surface which permit the enamel to combine with the material chemically or mechanically, or the elastic properties of the stock are so modified that the enamel is no longer crushed in cooling. Doubtless all factors play a salutary part. However this may be, the answer or solution by this method is the same regardless of the theory and is to treat mechanically the stock by stretching, cold rolling, spinning, shaping, or other means whereby all parts of the article are given the equivalent of the above.

In the preliminary microscopic studies of these mechanically treated samples, the ordinary methods were resorted to, that is, examination up to 100 magnifications of cross sections and surfaces. These magnifications proved unsatisfactory.

It was therefore decided to make some studies of the stocks at various magnifications from 200 to 2,000 diameters. On many specimens there is apparent under these magnifications a result of rolling or stretching which may account for its beneficial effect on the enameling properties and which may also account for the limited effect noted in the iron stock.

There has been noted in the case of some of the enameled cold rolled steels a rolling over of the tops of the peaks on the surface of the metal into the minute cavities on the surface in the direction of rolling, especially when examined under the high magnifications and perpendicular to the surface. The enamel, in melting, apparently flows back under these overhanging projections of metal and thus retains its grip on the latter in spite of the strain under which the enamel is compressed, because of the difference in expansion. Attempts are being made to reproduce such a structure artificially and in an exaggerated condition. The preliminary results of enameling such stocks are very encouraging.

In the case of the cold rolled iron, this broken cross section is not present to such marked degree. The surface has a more regular arrangement somewhat similar to that of normal steel. This is undoubtedly due to the greater ductility of the iron allowing the excess metal to be rolled down and united in the cavities, thus tending to nullify the beneficial effects of cold rolling noted in the case of the steels. In the stretched iron and steel, we should expect numerous cavities to be formed or opened up into which the enamel penetrates, which would account for the reduced fish scaling in the stressed iron and steel.

This broken structure was visible at 100 magnifications on the earlier stretched samples of steels and irons but, since the cold rolled steels C and D, at the same magnification, gave a very smooth appearance of surface, the value of the findings was consequently discounted at that time.

The microscopic studies of some sections of enameled iron and steel are shown in figures 6-9. Photographs of a specimen of steel partially cold rolled and enameled are shown in figure 11, while figure 10 shows a specimen of partially stressed steel which has

FIG. 10.—One-half of a steel strip stressed and enameled. Left half (N), normal; right half (S), stressed.

FIG. 11.—Strip, cold rolled and enameled. Left half (N), normal; right half (CR), cold rolled.

been enameled. In these there is apparent the sharp line of demarcation between the normal and the mechanically treated sections. The greater part of the scaling on the normal ends developed within 24 hours after enameling and these specimens were enameled about eight months previous to photographing. In the stressed section, a single scale is shown in the portion receiving the least stressing, since the specimen as photographed is one-half of the strip which was originally stretched.

Part II. Ground Coat Enamels

The second part of this investigation has been devoted to the study of ground coats in order to determine whether the general conclusions drawn from the study of gray ware would apply to three coat enamels.

An average composition was selected from the compositions of three commercial enamels, having various degrees of refractoriness and working properties but all giving good commercial ware. They are as follows in melted weights:

	A	B	C
Boric oxide.....	13.5	14.0	18.1
Feldspar.....	27.5	35.6	43.0
Quartz.....	34.7	25.4	21.6
Sodium oxide.....	11.6	15.8	11.6
Fluorspar.....	6.1	7.6	2.9
Manganese oxide.....	4.9	1.3	1.4
Nickel oxide.....	1.2		1.0
Cobalt oxide.....	0.5	0.3	0.4
	<hr/> 100.0	<hr/> 100.0	<hr/> 100.0

The average enamel selected for the work was as follows:

Constant

Feldspar.....	27
Quartz.....	21
Boric oxide.....	12
Sodium oxide.....	10
Fluorspar.....	0
Cryolite.....	0
Cobalt oxide.....	0.5
Manganese dioxide.....	1.5

72.0

Variable

Refractories.....	14.0
Fluxes.....	14.0

Total..... 100.0

With this composition as a basis the following three series shown in table 8 were outlined, an attempt being made to show the effect of varying the refractories as well as the fluxes as had been done in the study of the gray ware enamels. Ground coats H-1 to H-7 comprise a series with high content of feldspar showing variations in the fluxes. Group H-8 to 14 is a high quartz series and H-15 to 21 is a mean between the high quartz and high feldspar with similar variations in fluxes. The batch compositions are shown in table 9.

These ground coats, weighed in 4.5 lb. batches, were mixed thoroughly and then melted in crucibles in a crucible furnace. The time varied with the fusibility of the frit but averaged from 45 to 50 minutes. The frit in each case was chilled in water and then ground in porcelain ball mills with the following additions:

Frit.....	1200 gms.
Johnson Porter clay.....	72 gms.
Borax (in solution).....	18 gms.
Water.....	500 cc.

The time required for grinding averaged 12 hours but in this case it appeared that the time for grinding depended somewhat on the composition, the more fusible enamels requiring less time.

TABLE 8—PERCENTAGE COMPOSITION OF GROUND COAT FRITS

Constant part ingredients	Feldspar	Quartz	B ₂ O ₃	Na ₂ O	CaF ₂	Cryolite	Ox. of cobalt	Ox. of manganese
Constant part % ingredients melted	27	21	12	10	0	0	0.5	1.5
No. of ground Variable melted parts added to above constant portion								
H-1	14	..	7	..	7	..		
H-2	14	..	7	7	7	..		
H-3	14	..	..	..	7 + 7	..		
H-4	14	..	..	..	7	7		
H-5	14	..	7	..	..	7		
H-6	14	..	..	7	..	7		
H-7	14	..	..	..	..	7 + 7		
H-8	..	14	7	..	7	..	Constant	Constant
H-9	..	14	..	7	7	..		
H-10	..	14	..	..	7 + 7	..		
H-11	..	14	..	..	7	7		
H-12	..	14	7	..	..	7		
H-13	..	14	..	7	..	7		
H-14	..	14	..	..	..	7 + 7		
H-15	7	7	7	..	7	..		
H-16	7	7	..	7	7	..		
H-17	7	7	..	..	7 + 7	..		
H-18	7	7	..	..	7	7		
H-19	7	7	7	..	..	7		
H-20	7	7	..	7	..	7		
H-21	7	7	..	..	..	7 + 7		

TABLE 9—BATCH COMPOSITION OF GROUND COATS FOR 100 PARTS MELTED

Constant portion ingredients	Feldspar	Quartz	Borax	Boric Acid	Soda Ash	Sodium Nitrate	Fluor-spar	Cryolite	Cobalt Oxide	Manganese Oxide
Batch weights constant portion	27	21	32.7	—	5.0	4.9	—	—	0.5	1.5
No. of ground	Batch weight of variable parts added to above constant part									
H-1	14	..	..	12.4	..		7	..		
H-2	14	..	..		12		7	..		
H-3	14	..	..		..		14	..		
H-4	14	..	..		..		7	7		
H-5	14	..	..	12.4	..		..	7		
H-6	14	..	..		12		..	7		
H-7	14	..	..		..		..	14		
H-8	..	14	..	12.4	..		7	..		
H-9	..	14	..		12		7	..		
H-10	..	14	..		..	Constant	14	..	Constant	Constant
H-11	..	14	..		..		7	7		
H-12	..	14	..	12.4	..		..	7		
H-13	..	14	..		12		..	7		
H-14	..	14	..		..		..	14		
H-15	7	7	..	12.4	..		7	..		
H-16	7	7	..		12		7	..		
H-17	7	7	..		..		14	..		
H-18	7	7	..		..		7	7		
H-19	7	7	..	12.4	..		..	7		
H-20	7	7	..		12		..	7		
H-21	7	7	..		..		..	14		

These were applied to a number of steels, the sample plates being 2 × 3 inches and of 16, 20 and 24 gauge. The steel was prepared by cleaning in an alkaline bath and pickling in hydrochloric acid. The plates were then rinsed in water and the remaining acid neutralized in a weak soda-ash bath.

Enamels were applied by dipping, additional borax being used as a flotation medium when necessary.

In order to obtain the effect of various temperatures on fish scaling, each of the ground coats were fired on six plates according to the following schedule:

Degrees C	Minutes
800	2 $\frac{1}{2}$
850	1 $\frac{3}{4}$
900	1 $\frac{1}{4}$

Firing according to this schedule gave to all appearances, correctly fired enamels. Half of these plates were then coated with a standard white enamel of the following composition:

Frit		Mill	
Borax.....	500	Frit.....	100
Feldspar.....	640	Clay.....	5
Quartz.....	360	Tin oxide...	7
Soda ash	80	Magnesia...	$\frac{1}{4}$
Cryolite.....	240	Water.....	50
Soda nitre.....	60		
Antimony oxide.....	40		
Fluorspar.....	80		
Total.....	2000		

The general results on the ground coat enamels are in general accord with those of the gray ware studies. For example, we find in a study of the data that the enamel constituents arrange themselves in the same order as affecting fish scaling, that is, cryolite is a superior flux to fluorspar, boric acid is an exceedingly poor flux from the standpoint of fish scaling, and soda and cryolite are much alike in their beneficial effects. It is to be noted further in this work that feldspar is apparently superior to flint.

Of the 21 enamels only one, H-6, has not developed fish scaling under any condition. This approaches very closely a type of commercial ground coat except that cryolite replaces the usual amount of fluorspar present in ground coats. It is to be noted further that the corresponding enamels in the quartz as well as in the medium-quartz medium-feldspar series (H-13 and H-20), are the best in these respective series and approach the excellent qualities of H-6. Boric oxide as in the case of the gray ware enamels is harmful from the standpoint of fish scaling. It is to be noted that better results are obtained with ground coats H-1 to 7, followed in order by H-15 to 21 and then H-8 to 14. This is undoubtedly due to the fact that the first group is highest in feldspar which we would expect to give tougher enamels in the range of compositions listed and is further evidence that the strength of the enamel is a factor in the tendency to fish scale.

The results of the expansivity studies confirm the conclusions from similar studies of the gray ware enamels and give further proof of the accuracy of our basic reason for the phenomenon of fish scaling. The coefficient values shown in tables 10 and the expansivity charts showing cooling curves for Enamels H-1 to 14, (figures 12 and 13) as compared with and matched to steel at 450°C, make this evident. It will be recalled that the gray ware enamels were matched with the stock at 500°C on the basis of tests

FIG. 12 —Expansion of ground coats H-1 to 18 and stock.

which showed that the gray ware enamels became viscous at approximately 550°C . It was found, however, that the ground coats softened at about 500°C and it was therefore necessary to lower the assumed temperature for initial rigidity of enamel and to fit the stock and grounds at 450°C . The following general conclusions can be drawn from the expansivity studies:

(1) Feldspar, replacing corresponding amounts of flint as a refractory, gives higher values for the expansion coefficient than the flint.

FIG. 13.—Expansion of ground coats H-8 to 14 and stock.

- (2) Cryolite gives higher values on the average than fluorspar.
- (3) Boric acid gives the lowest values.
- (4) Sodium oxide and cryolite combinations give the highest values followed by that for cryolite alone.

The fusion points of these ground coats place the various fluxes in their same relative order as regards fluxing value (figure 14), as observed for the gray ware enamels. The cone method of determining fusion points was not applicable to the ground coats

FIG. 14.—Relative fusibilities of ground coats.

as the fluxes separating out from the refractories tended to give erratic results. These softening points were, therefore, determined by placing pats of enamel on a plate and heating for two minutes at various temperatures.

The results of tests of shape of ware, annealing of enameled ware, treating of the steel, and so forth, have all corroborated the results obtained with gray ware enamels so it would appear that the conclusions can be applied generally to sheet steel enamels.

TABLE 10—COEFFICIENTS OF EXPANSION $\times 10^6$. GROUND COAT
ENAMELS AND STEELS

Ground	Room to 200°C	Room to 400°C	Room to 450°C
H-1	9.2	10.3	10.5
H-2	9.4	10.3	11.5
H-3	8.4	10.4	12.1
H-4	9.7	10.9	12.3
H-5	8.3	10.0	11.4
H-6	9.7	10.9	12.6
H-7	9.8	11.2	12.5
H-8	7.5	8.4	8.9
H-9	8.9	10.3	11.2
H-10	8.8	9.5	10.0
H-11	8.8	10.3	11.5
H-12	8.2	9.4	10.7
H-13	9.1	11.5	13.3
H-14	9.5	10.8	12.3
Av. Steel	12.8	14.0	14.2