

## GROUND COAT ENAMELS FOR CAST IRON.<sup>1</sup>

By HOMER F. STALEY, Ames, Iowa.

The function of a ground coat enamel is that it should serve as a bond between the cover enamel and the iron and also protect the iron from oxidation while being heated to the temperature at which the cover enamel fuses. Statements are sometimes found in the literature that a ground coat is not necessary when powdered enamels are used for cast iron.<sup>2</sup> While it is sometimes possible to enamel a trial piece without the use of a ground coat, the percentage of good pieces obtained in this way is very small and the process is not a commercially feasible one. At the present time ground coats are universally used in the enameling of cast iron in this country.

It was formerly the practice to use very refractory ground masses which were merely sintered onto the iron but were not fused to a glass. The object was to produce a porcelain-like coating on the metal, toward which the cover enamel would act as a glaze. This type of ground coat is still used for wet-coat enamels on cast iron but for the powdered enamels it has been superseded to a large extent by thin glossy ground coats.

The basis of these sintered ground coats was a frit prepared from flint and borax, or from flint, feldspar and borax, with small additions of lead or sodium oxides. To this frit, clay and flint, or clay and feldspar, were added in sufficient quantities to make the refractoriness of the mass such that it would sinter, but not fuse in the enameling oven. Magnesium oxide or sulphate was used in small quantities to assist in floating the enamel. The ground coat was fired until it could not be rubbed off with the fingers and until the individual grains appeared rounded when

<sup>1</sup> By permission of the Director, Bureau of Standards.

<sup>2</sup> Holdcroft, H., *Jour. Soc. Chem. Ind.*, **29**, 123.

examined with a good hand glass.<sup>1</sup> Formula No. 1 is a ground coat of this type which has been used in this country in the preparation of wet coat enamels. Further examples can be found in *Randau*, pages 124 and 125.

In the use of glassy ground coats, enamel makers have discarded the idea of there being an analogy between the enameling of cast iron and the glazing of porcelain and have attempted to produce glasses that would afford the maximum adhesion between the enamel and the metal. A satisfactory ground coat of this class should melt at a dull red heat, in order to protect the iron from oxidation; should be able to dissolve any oxides or foreign matter on the surface of the metal; should be sufficiently fluid to flow in part, into the minute pores of the metal, so as to produce a good bond, and should not blister or volatilize (burn off) until temperatures above those commonly employed in enameling furnaces are reached.<sup>2</sup>

The mixtures commonly employed in preparing the frits for this type of enamel are flint or sand, feldspar, borax, red lead and sodium nitrate. Flint and feldspar are the refractory ingredients of the enamel and supply the silica essential to the production of a permanent glass. Flint or sand is often used alone as the refractory component, especially in the older formulae, but many recipes call for the use of some feldspar in addition to the flint. Borax is used in the largest proportions as a flux on account of the ability of boric oxide to dissolve iron and other oxides. A ground coat glass high in boric oxide readily dissolves any small amounts of iron oxide present on the surface of the iron. Lead oxide is used because its compounds melt at low temperatures and produce fluid glasses having good mechanical strength when cold. The small amount of sodium nitrate is introduced in order to secure the oxidizing effect of the nitrate radical which prevents the reduction of the lead and the absorption of injurious sulphur gases by the glass during the fritting process. Small amounts of other fluxes such as fluorspar, cryolite,

<sup>1</sup> Paul Randau, "Enamels and Enameling," 2nd English edition, pp. 20 and 148, Scott Greenwood & Co.

<sup>2</sup> *Trans. Am. Ceram. Soc.*, 13, 531 (1911).

barium oxide, soda ash, etc., are sometimes used, but these perform no distinctive service and most of the enamel frits are compounded from the above list of materials. Small amounts of magnesium carbonate and magnesium sulphate are sometimes used in enamel frits on the assumption that they aid in the adhesion of the ground coat to the iron.<sup>1</sup> Cobalt oxide in small amounts is employed in many enamel frits for the same purpose.

As a raw material to be added at the mill, clay is invariably used on account of its ability to cause the enamel composition as a whole to remain in suspension. It also serves as a refractory ingredient and, in some cases, is the only raw refractory material introduced. Flint and feldspar are occasionally used as raw refractories. Magnesium carbonate, magnesium sulphate, borax, lime water, ammonia, etc., are used in small amounts to assist in floating the enamel. Sometimes a little raw cobalt oxide is added in cases where it has not been convenient to include in the frit.

The function and value of cobalt oxide in ground coats for cast iron is a debatable question. After a careful investigation of the subject, Coe came to the conclusion that "the use of cobalt oxide in a ground coat for cast iron enamels is of doubtful value."<sup>2</sup> On the other hand, manufacturers of sheet steel enamels in general claim that they cannot produce a satisfactory ground coat without the use of cobalt oxide or some other metallic oxide as a substitute for the cobalt. The remarkable effects claimed for the very small amounts of cobalt oxide added are not accounted for, and various unproven theories are advanced in an attempt to explain the phenomena.<sup>3</sup>

Since many excellent ground coats contain no cobalt, it is evident that cobalt oxide is not essential to the production of a satisfactory ground coat for cast iron. On the other hand, various factors enter into the production of satisfactory enameled iron ware and it is very difficult to determine the effect of the presence of cobalt oxide in the ground coat. As a result many

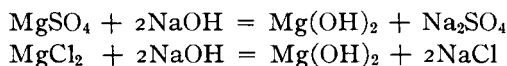
<sup>1</sup> Paul Randau, "Enamels and Enameling," p. 126.

<sup>2</sup> *Trans. Am. Ceram. Soc.*, 13, p. 545 (1911).

<sup>3</sup> R. D. Landrum, *Ibid.*, 14, pp. 756-763 (1914).

enamellers, including the writer, in some instances use cobalt oxide in the preparation of ground coats because they feel that it is not detrimental and may possibly be beneficial. The cost of the cobalt oxide, compared to the value of the ware produced, is so small that its elimination from the formulas is not advisable.

As demonstrated by Ernest Mayer for glazes,<sup>1</sup> the settling of enamels is due to an excessive alkalinity of the enamel solution. Mayer divides the materials used for the flotation of slips into those whose action is physical and those whose action is chemical. In the first group are clay, syrup, gum arabic, dextrine, milk and blood. The two latter soon curdle and make quite thick suspensions. In the chemical group are various acid substances, including boric acid, vinegar, hydrochloric and sulphuric acid, which reduce the alkalinity by neutralizing a part of the alkali. A more effective group of chemicals are those which neutralize a part of the alkalinity and at the same time produce a flocculent precipitate. The most commonly employed are magnesium sulphate and magnesium chloride:



It is a noteworthy fact that not one of these chemical vehicles has any appreciable coagulating effect unless clay is present. It would appear, therefore, that the effect of these reagents is to coagulate the clay and thus render it capable of floating the other enamel ingredients. By the addition of acid substances, the enamel suspension would be rendered acid or faintly alkaline, a condition which is favorable to coagulation. By the addition of magnesium salts, the alkalinity would be reduced, a flocculent precipitate,  $\text{Mg}(\text{OH})_2$ , would result, and a coagulating salt, sodium sulphate or chloride, would remain in solution. Ammonium carbonate is a very effective coagulant while borax serves as a coagulant or deflocculent according to the conditions. The other chemicals used for the floating of enamels are capable of flocculat-

<sup>1</sup> *Trans. Am. Ceram. Soc.*, **11**, 369 (1909).

ing the clay under the proper conditions and we have every reason for assuming that this is their mode of action.<sup>1</sup>

As pointed out by Mayer, it is theoretically a mistake to introduce a sulphate, such as magnesium sulphate, into a ground coat on account of the danger of the development of sulphur blisters. However, magnesium sulphate is the most commonly employed vehicle with the exception of clay, and apparently the small amounts added are not harmful. Greenwald recommends the addition of magnesium oxide (calcined magnesium carbonate) and ammonium carbonate as being chemically harmless.<sup>2</sup>

Magnesium oxide and carbonate, calcium oxide, calcium hydroxide (milk of lime) and calcium carbonate, may cause serious difficulties if deposited upon the ware in large granules. These granules will not be melted into the ground coat or enamel but burn to particles of quicklime ( $\text{CaO}$  or  $\text{MgO}$ ). In the course of several months some of these particles will hydrate, the moisture presumably working through the porous iron with which they are in contact, and expand. This causes the enamel above them to break off in little cone-shaped spalls. This liability is not an imaginary one, for the writer has inspected ware to the value of twenty thousand dollars, in one stockroom, ruined in this manner. For this reason it is preferable to eliminate the insoluble compounds of magnesium or calcium as vehicles for floating the enamels.

The so-called "vehicles" may be added when the ground coat is charged into the mill, but the more common practice is to add the clay just previous to the grinding and to add the others to measured quantities of the ground coat just before its application. When vehicles other than clay are used, the consistency of a ground coat varies greatly with age.

The most simple and oldest type of glassy ground coat consists of a refractory frit, high in sand or flint and generally containing cobalt, to which only enough clay to float it is added at the mill. Ground coats Nos. 2 and 3 are typical formulas, showing the range of lead oxide and borax commonly employed in this type

<sup>1</sup> H. E. Ashley, "Technical Control of the Colloidal Matter in Clays," *Bur. Standards, Tech. Paper*, 23, 74-102.

<sup>2</sup> *Speersaal*, 43, 594.

of ground coat. The variations in cobalt oxide are also within the normal limits. Ground coats containing a high percentage of borax are more popular than those high in lead oxide, and formulas similar to No. 2 are in more common use than those similar to No. 3.

With the general adoption, in late years, of feldspar cover enamels, it is quite natural that feldspar should have been introduced into ground coat frits. The feldspar has not replaced flint and sand entirely as in many cover enamels—a formula for a ground coat containing neither flint nor sand being very unusual.

With the introduction of frit kilns it was not advisable to include the cobalt in the ground coat frit, as the kiln could not be used for both the white and colored enamels. Consequently, in some modern formulas we find cobalt oxide as an addition to be made at the mill. No. 4 is a typical ground coat formula containing feldspar in the frit, the cobalt being added at the mill.

It was quite natural that, from time to time, enamel mixers should attempt the blending of two ground coats. In some cases the results were so satisfactory that the use of a formula calling for the blending of two ground coats became an established factory practice. According to the results obtained by J. H. Coe,<sup>1</sup> in some cases the blending of two ground coats having about the same heat range will produce coats having longer heat ranges than is obtained by the use of either coat alone. No. 5 is a typical ground coat formula of this kind. Incidentally it calls for the addition of raw magnesium carbonate.

In the four glassy ground coat formulas already given, the frits themselves are quite refractory and comprise the bulk of the coat. The raw material consists essentially of only sufficient clay to float the enamel. In late years, since the rather general use of frit kilns for the smelting of ground coat frits, the use of formulas containing more fusible frits and larger amounts of refractory raw additions has been practiced in a number of plants. Formula No. 6 is typical of a number of ground coats in use

<sup>1</sup> *Trans. Am. Ceram. Soc.*, 13, 531-549 (1911).

which contain large amounts of clay as the raw refractory addition. One advantage of this type of formula is that the use of chemical "vehicles" for floating the coats can be avoided.

The use of clay alone as the raw refractory, in case the amount to be added is large, is not as common as the employment of a small or moderate amount of clay as a floating agent and the addition of either flint or feldspar, or both, as refractory ingredients. No. 7 is a formula of a ground coat calling for clay, flint and feldspar as the raw additions. In this formula two frits are blended, the effect being the same as the blending of two ground coats. This ground coat is more fusible than the preceding ones, being employed in the enameling of light castings.

It is somewhat difficult to estimate the comparative fusibilities of a series of enamel formulas, whether these be presented in the proportions of the raw batch, percentage composition, or empirical chemical formulas. When only one refractory ingredient is used, some idea of the fusibility may be obtained by observing the percentage of the refractory addition in the melted enamel. For this reason, in submitting the composition of cover coat enamels, we have employed formulas calling for potash feldspar as the only refractory. It is impossible to follow this practice in ground coat enamels, for the clay, flint and feldspar must be taken into consideration.

By practical trial the writer has determined that, in cast iron enamels, the potash, feldspar, flint and clay may be substituted for one another without changing the fusibility of the enamel, the ratio being 100 feldspar :  $66\frac{2}{3}$  flint : 40 clay.<sup>1</sup> By assuming that flint is substituted in these ratios for all of the clay and feldspar contents in each of the ground coat formulas given here and by reducing the batch to 1000 pounds (melted), we obtain a number indicating the pounds of flint that would have been used for 1000 pounds of the ground coat melted, if the only refractory employed had been flint. We have called this number the "flint equivalent" of the formula. The flint equivalent of a ground coat gives a fair indication of its refractoriness, for variation in the amount of the flint added has such a decided effect

<sup>1</sup> *Trans. Am. Ceram. Soc.*, 13, 505 and 534 (1911).

that the influence of variations commonly found in the relative amounts of the fluxing oxides may be neglected.

Ground coat No. 1 is quite refractory and has a high "flint equivalent." Ground coat No. 7 is quite fusible and has a correspondingly low "flint equivalent." Ground coats Nos. 2 to 6 are supposed to be well adapted to general lines of enameled iron wares. It is remarkable how nearly uniform are the "flint equivalents" of these five recipes obtained from various sources.

### Ground Coat No. 1.

Batch for 1000 pounds.					Percentage composition.
Frit.	Raw.	Melted.			
Flint.....	350.0		SiO <sub>2</sub> .....	77.83	} 84.99
Borax .....	185.0		Al <sub>2</sub> O <sub>3</sub> .....	7.16	
Sodium nitrate...	35.0		Na <sub>2</sub> O.....	4.28	
Red lead.....	41.0		B <sub>2</sub> O <sub>3</sub> .....	6.77	
			PbO.....	4.00	
	611.0	500.0			100.04

#### Additions.

Flint.....	345.0	345.0
Clay.....	180.0	155.0
	1136.0	1000.0

"Flint equivalent" = 869

#### EMPIRICAL CHEMICAL FORMULA.

$$\begin{array}{l}
 0.785 \text{ Na}_2\text{O} \\
 0.215 \text{ PbO}
 \end{array}
 \left. \vphantom{\begin{array}{l} 0.785 \text{ Na}_2\text{O} \\ 0.215 \text{ PbO} \end{array}} \right\}
 0.807 \text{ Al}_2\text{O}_3
 \left\{ \begin{array}{l} 14.743 \text{ SiO}_2 \\ 1.103 \text{ B}_2\text{O}_3 \end{array} \right.$$

1.000



## Ground Coat No. 2.

Batch for 1000 pounds.					Percentage composition.
Frit.	Raw.	Melted.			
Flint.....	675.0		SiO <sub>2</sub> .....	70.28	72.67
Borax.....	390.0		Al <sub>2</sub> O <sub>3</sub> .....	2.39	
Sodium nitrate...	35.0		Na <sub>2</sub> O.....	7.60	
Red lead.....	52.5		B <sub>2</sub> O <sub>3</sub> .....	14.27	
Cobalt oxide.....	3.0		PbO.....	5.15	
			CoO.....	0.30	
	1155.5	948.0			99.99
Addition.					
Clay.....	60.0	52.0			
	1215.5	1000.0			
"Flint equivalent" = 735					

## EMPIRICAL CHEMICAL FORMULA.

$$\begin{array}{l}
 0.810 \text{ Na}_2\text{O} \\
 0.165 \text{ PbO} \\
 0.025 \text{ CoO}
 \end{array}
 \left. \vphantom{\begin{array}{l} 0.810 \\ 0.165 \\ 0.025 \end{array}} \right\}
 0.158 \text{ Al}_2\text{O}_3
 \left\{ \begin{array}{l} 7.705 \text{ SiO}_2 \\ 1.342 \text{ B}_2\text{O}_3 \end{array} \right.$$

1.000

## Ground Coat No. 3.

Batch for 1000 pounds.					Percentage composition.
Frit.	Raw.	Melted.			
Flint.....	680.0		SiO <sub>2</sub> .....	70.36	72.39
Borax.....	170.0		Al <sub>2</sub> O <sub>3</sub> .....	2.03	
Sodium nitrate...	50.0		Na <sub>2</sub> O.....	4.57	
Red lead.....	170.0		B <sub>2</sub> O <sub>3</sub> .....	6.26	
Cobalt oxide.....	0.85		PbO.....	16.66	
			CoO.....	0.085	
	1070.85	956.0			99.97
Addition.					
Clay.....	51.0	44.0			
	1121.85	1000.0			
"Flint equivalent" = 735					

## EMPIRICAL CHEMICAL FORMULA.

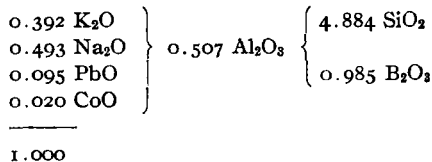
$$\begin{array}{l}
 0.448 \text{ Na}_2\text{O} \\
 0.485 \text{ PbO} \\
 0.067 \text{ CoO}
 \end{array}
 \left. \vphantom{\begin{array}{l} 0.448 \\ 0.485 \\ 0.067 \end{array}} \right\}
 0.121 \text{ Al}_2\text{O}_3
 \left\{ \begin{array}{l} 7.102 \text{ SiO}_2 \\ 0.539 \text{ B}_2\text{O}_3 \end{array} \right.$$

1.000

## Ground Coat No. 4.

Batch for 1000 pounds.					Percentage composition.
Frit.	Raw.	Melted.			
Sand.....	275.0		SiO <sub>2</sub> .....	58.30	} 68.57
Potash feldspar...	435.0		Al <sub>2</sub> O <sub>3</sub> .....	10.27	
Borax.....	375.0		K <sub>2</sub> O.....	7.35	
Red lead.....	41.0		Na <sub>2</sub> O.....	6.07	
			B <sub>2</sub> O <sub>3</sub> .....	13.72	
	1126.0	948.0	PbO.....	4.00	
			CoO.....	0.30	
			<hr/>		
			100.01		
Additions.					
Clay.....	57.0	49.0			
Cobalt oxide.....	3.0	3.0			
	1186.0	1000.0			
"Flint equivalent" = 733					

## EMPIRICAL CHEMICAL FORMULA.



## Ground Coat No. 5.

Blue ground coat. Batch for 1000 pounds.			White ground coat. Batch for 1000 pounds.		
Frit.	Raw.	Melted.	Frit.	Raw.	Melted.
Sand.....	685.0		Sand.....	395.0	
Borax.....	335.0		Potash feldspar.....	315.0	
Sodium nitrate.....	30.0		Borax.....	335.0	
Red lead.....	85.0		Sodium nitrate.....	30.0	
Cobalt.....	2.7		Red lead.....	60.0	
	1137.7	958.0		1135.0	958.0
Additions.					
Clay.....	48.0	41.0	Clay.....	48.0	41.0
Magnesium carbonate	3.0	1.5	Magnesium carbonate	3.0	1.5
	1188.7	1000.5		1186.0	1000.5
"Flint equivalent" = 734			"Flint equivalent" = 730		

The final ground coat is made by taking two parts of blue ground coat and one part of white ground coat. This gives a flint equivalent of 733.

Percentage composition.	
SiO <sub>2</sub> .....	67.82
Al <sub>2</sub> O <sub>3</sub> .....	3.80
K <sub>2</sub> O.....	1.77
Na <sub>2</sub> O.....	6.66
B <sub>2</sub> O <sub>3</sub> .....	12.13
PbO.....	7.50
MgO.....	0.14
CoO.....	0.18
<hr/>	
100.00	

EMPIRICAL CHEMICAL FORMULA.

0.115 K <sub>2</sub> O	}	0.224 Al <sub>2</sub> O <sub>3</sub>	{	6.827 SiO <sub>2</sub>
0.646 Na <sub>2</sub> O				
0.021 MgO				
0.203 PbO				1.033 B <sub>2</sub> O <sub>3</sub>
0.015 CoO				
<hr/>				
1.000				

Ground Coat No. 6.

Batch for 1000 pounds.			Percentage composition.	
Frit.	Raw.	Melted.		
Sand.....	200.0		SiO <sub>2</sub> .....	48.00
Feldspar.....	200.0		Al <sub>2</sub> O <sub>3</sub> .....	16.61
Borax.....	390.0		K <sub>2</sub> O.....	3.38
Sodium nitrate.....	30.0		Na <sub>2</sub> O.....	7.42
Red lead.....	100.0		B <sub>2</sub> O <sub>3</sub> .....	14.27
Magnesium carbonate...	10.0		PbO.....	9.80
			MgO.....	0.48
	930.0	720.0	CoO.....	0.10
				100.06
Additions.				
Clay.....	325.0	279.0		
Cobalt oxide.....	1.0	1.0		
	1256.0	1000.0		

"Flint equivalent" = 732

## EMPIRICAL CHEMICAL FORMULA.

0.167 K <sub>2</sub> O	}	0.758 Al <sub>2</sub> O <sub>3</sub>	{	3.72 SiO <sub>2</sub>
0.553 Na <sub>2</sub> O				
0.056 MgO				0.95 B <sub>2</sub> O <sub>3</sub>
0.219 PbO				
0.005 CoO				
<hr/>				
1.000				

## Ground Coat No. 7.

Batch for 1000 pounds.

Frit. No. 1.	Raw.	Melted.		Percentage composition.
Potash feldspar.....	300.0		SiO <sub>2</sub> .....	50.63
Borax.....	115.0		Al <sub>2</sub> O <sub>3</sub> .....	10.71
Sodium nitrate.....	20.0		K <sub>2</sub> O.....	7.10
Red lead.....	125.0		Na <sub>2</sub> O.....	4.36
			B <sub>2</sub> O <sub>3</sub> .....	6.95
			PbO.....	20.30
	<hr/>			<hr/>
	490.0			100.05

Frit No. 2.

Flint.....	125.0
Borax.....	75.0
Sodium nitrate.....	15.0
Red lead.....	82.0
	<hr/>
	250.0

Additions.

Clay.....	75.0	65.0
Flint.....	75.0	75.0
Feldspar.....	120.0	120.0
	<hr/>	<hr/>
	1127.0	1000.0

"Flint equivalent" = 658

## EMPIRICAL CHEMICAL FORMULA.

0.31 K <sub>2</sub> O	}	0.428 Al <sub>2</sub> O <sub>3</sub>	{	3.444 SiO <sub>2</sub>
0.29 Na <sub>2</sub> O				
0.40 PbO				0.404 B <sub>2</sub> O <sub>3</sub>
<hr/>				
1.00				

## DISCUSSION.

MR. LANDRUM: In the percentage composition given, do you include the mill mix or is it merely the batch mix?

PROF. STALEY: That is a calculated percentage composition.

MR. LANDRUM: But does it include the addition at the mill?

PROF. STALEY: Yes.

MR. LANDRUM: And does the empirical formula also include the mill addition?

PROF. STALEY: Yes.

MR. LANDRUM: Ground coat No. 7 is very similar to a sheet steel ground coat.

MR. POSTE: I have been interested in some of the work Prof. Staley has carried out in the past, relative to the possible substitution of one refractory for another and producing the same fusibility. An interesting point is that this "flint equivalent" is apparently the outgrowth of that work. I assume that the work done heretofore was derived from actual experiment and has been verified in practice. This is a much more complicated case of the same thing. Is it practicable?

PROF. STALEY: This was not tried out at all. These are formulas which were obtained from various sources. I calculated the "flint equivalent" from the factory formulas. In five formulas, supposedly used for general sanitary work, bathtubs, etc., the "flint equivalent" was about the same and we had every reason for assuming that about the same temperature is employed in most factories in maturing the ground coats. These were not made up in order to verify the "flint equivalent." I calculated the "flint equivalent" after the enamel had actually been used in the factory.

MR. POSTE: What would be the effect of replacing the feldspar and other refractory materials by the theoretical amount of flint? Have you determined this experimentally?

PROF. STALEY: Yes.

MR. POSTE: What were the results as compared to those of the previous experimental work?

PROF. STALEY: I operated a factory for four years on that basis, that is, substituting one material for another on the basis of experimentally determined equivalents.

MR. POSTE: The old question of cobalt in the ground coat is always interesting to us, and one little piece of experimental work we were conducting a while ago brought forth the very interesting proof of one theory; that under certain conditions in steel ground coats containing cobalt oxide, metallic cobalt actually separates and alloys with the steel. We happened to be doing some fundamental work, involving mixtures which included no oxidizing materials whatever, but containing cobalt oxide. After withdrawing the stirring rod from the molten batches containing no oxidizing material, there was a peculiar glossy coating on the surface of the rod. It appeared to be metallic cobalt. We sawed off the end of this rod and found that metallic cobalt had been deposited. We were endeavoring to determine the effect of nitrates and we substituted increasing amounts of nitrates for carbonates without varying the  $\text{Na}_2\text{O}$  content, and the tendency of the cobalt to deposit on the steel rod gradually disappeared, indicating that the oxidizing material kept it in the oxidized form and in the absence of an oxidizing material it was reduced, a deposit of metallic cobalt forming on the surface of the rod.