VITREOUS ENAMELING OF IRON AND STEEL

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READING LIST

ON

VITREOUS ENAMELING OF IRON AND STEEL

Compiled by

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A READING LIST ON VITREOUS ENAMELING ON IRON AND STEEL

The literature of the ceramic industry is very well covered up to the year 1906 by the Bibliography of Clays and the Ceramic Arts compiled by John C. Branner. The following reading list, therefore, begins with the year 1907. The articles listed deal more with the chemical principles involved than with mechanical methods. References are given to the abstracts printed in Chemical Abstracts or in the Journal of the Society of Chemical Industry. These abstracts are reproduced in part below, though where the abstract is long, or where the title indicates the scope of the article, abstracts are usually omitted. Reference to abstracts will enable the investigator to eliminate many articles as being unsuitable for his particular purpose. United States patents on enameling are omitted, as they are given in the second part of this pamphlet. Directions for ordering foreign patents may be found in Chemical Abstracts, vol. 13, no. 6 (March 20, 1919).

BOOKS

Chapin, H. M. How to enamel. 1911. Wiley.
Fisher, A. Art of enameling upon metals. 1906. Lane. 38 pages, 26 plates.
Franchet, L. La fabrication industrielle des émaux et couleurs céramiques. 1911.
Griffin, H. R. Clay glazes and enamels, with a supplement on crazing, its causes and prevention, 1913. Randall and Co.
Millenet, L. Manuel pratique de l’emaillage sur metaux. 1917.
Turner, William. Transfer printing on enamels, porcelain and pottery.

ARTICLES IN PERIODICALS

1907


Klissner, J. Kiln for enameled articles, in which these do not come in contact with the flame. German Patent 203,296. Apr. 10, 1907. J. Soc. Chem. Ind., 27, 1204.

Riddle, F. H. The type of enamel used for enameling cast iron sanitary ware. *Trans. Amer. Ceram. Soc.*, 9, 645-61 (1907); *C. A.*, 2, 1483; *J. Soc. Chem. Ind.*, 27, 565. The most favorable composition was found to be: 0.4 PbO and BaO, 0.15 K₂O, 0.15 CaO, 0.05 ZnO, 0.25 Na₂O, 0.15 Al₂O₃, 1.0 SiO₂, 0.2 B₂O₃, 0.2 SnO₂.


1908


Bock, B. Note on white antimony enamels. *Chem.-Ztg.*, 32, 446-7 (1908); *C. A.*, 2, 2132; *J. Soc. Chem. Ind.*, 27, 566. Dangers are pointed out, owing to the ready solubility and the poisonous character of the compounds of antimony. Slow cooling of frits in place of the rapid quenching is advised.


Enameling of sheet iron hollow ware. *Keram. Rundschau*, 16, 89-91, 135-9 (1908); *C. A.*, 2, 1605. Various formulas are given in which zirconium is replacing tin.


Franchet, Louis. The enamels and ceramic colors of the Middle Ages and the Renaissance. *La Ceramique*, 10, 142; *C. A.*, 2, 2609. Various compositions are given.


Landau et Cie., and Rosenzweig, C. White enamel of great covering power. French Patent 389,483, Apr. 22, 1908. *C. A.*, 4, 2720; *J. Soc. Chem. Ind.*, 27, 983; *La Ceramique*, 11, 100-1; *C. A.*, 3, 364. Silicates of zirconium and beryllium are used in place of tin, etc. They are more refractory, more resistant to acids and are cheaper.


Vollkommer, Joseph. Furnaces for the enameling industry. Iron Age, 82, 648-9 (1908); C. A., 2, 2981.


Woog, P., and Delage, M. Process of enameling in one stage. French Patent 401,543, July 29, 1908. J. Soc. Chem. Ind., 28, 1130. An acetylene flame is directed onto the spot where the enamel is required and the finely ground enamel is also projected on the same spot.

1909

Bock, B. Fixation materials in enamel making. Chem.-Ztg., 33, 109 (1909); C. A., 3, 1450. Fixation materials are those substances which have the effect of holding the fine enamel glass particles in suspension, thus preventing their settling to the bottom of the mass after fusion. These include clay; insoluble magnesium salts; soluble, neutral salts, such as ammonium chloride (volatile), alkali carbonates and sulfates (partly volatile), and borax (non-volatile).

Colin, G., et Cie. Process of enameling cast iron articles and especially pots and cooking utensils. French Patent 411,630, Apr. 14, 1909. J. Soc. Chem. Ind., 29, 951. The interior of the pots is polished and then oxidized into a layer of magnetic oxide of iron, to which the enamel is applied by the wet process and as liquid as possible.


Grünwald, Julius. Note on the technology of the enameling industry. Oesterr. Chem. Ztg., 11, 271; C. A., 3, 2364. The density of certain enamels is given, with and without water. Certain analytical methods are also given.

Lesmuller, A. Process for making glass and enamels opaque. German Patent 218,316, April 1, 1909. J. Soc. Chem. Ind., 29, 420. Oxides of tin, silicon, lead, titanium, zirconium or thallium are fused with boric acid derivatives and the fused mass exposed to the action of steam or acid vapors while it cools and the solid product subsequently melted with the enamel.


Mayer, M., and Havas, B. The function of fluorine compounds in enamels. Sprechsaal, 42, 460–1 (1909); Chem.-Ztg., 33, 758 (1909); C. A., 3, 2740, 3001; J. Soc. Chem. Ind., 28, 835. Fluorine is a good opacifier and permits the tin oxide to be decreased to 3 per cent and still maintain excellent covering power.


1910


Grünwald, J. The stiffening of wet ground enamels. Sprechsal, 43, 594–7 (1910); C. A., 5, 168; J. Soc. Chem. Ind., 29, 1251. The reagents recommended are ammonium chloride or carbonate, magnesium oxide and borax.

VITREOUS ENAMELING

Holcroft, Harold. The principles of vitreous enameling of cast iron for industrial purposes. *J. Soc. Chem. Ind.*, 29, 121-5 (1910); *C. A.*, 4, 1227. Four methods are discussed.


Tafner, H. Fluorite and its function in enamels. *Sprechsaal*, 43, 36-7 (1910); *C. A.*, 5, 773; *J. Soc. Chem. Ind.*, 29, 213. Enamels containing calcium fluoride do not represent stable compounds as fluorine continues to be given off on heating.


1911

Cothen. The training of engineers for enamel works at Friedrich-Polytechnicum. *Glashütte*, 41, 309-10; *C. A.*, 5, 2711.


Deutsche Stahlhottich Ges. Subsequent enameling of rough places and weld-

Eyer, Ph. How much of the heat applied to enamel firing and melting ovens is useful? *Glashütte*, 41, 931–2; C. A., 6, 415.


Doubt is expressed as regards the efficiency of zirconium oxide as an opacifier.

Havas, B. The function of the ground enamel. *Sprechsaal*, 44, 72–3 (1911); C. A., 5, 2163.

Landau et Cie, and Rosenzweig, C. White enamels. English Patent 10,418, Apr. 29, 1911. French Patent 429,665, May 12, 1911. C. A., 6, 2986; *J. Soc. Chem. Ind.*, 30, 1213; *La Ceramique*, 14, 204. A part of the silicate of either the natural or artificial silicate of zirconium is removed by warming with alkali carbonate or hydroxide, which product is very suitable for rendering enamels opaque.


Mayer, M., and Havas, B. Reactions during the fusion of iron enamels (containing fluorine). *Sprechsaal*, 44, 6–8 (1911); C. A., 5, 2163; *J. Soc. Chem. Ind.*, 30, 930.

Meyer, A. Enameling or glazing plates of iron, steel, etc. German Patent 266,161, July 9, 1911. C. A., 8, 809.


Rickmann, R. White pigments for enamels, etc. German Patent 283,204, Dec. 5, 1911. *C. A.*, 9, 2444. Substances containing antimony are used.


Schott, E. A. Muffle oven for enamel works and other industrial purposes. *Stahl u. Eisen*, 31, 310 (1911); *C. A.*, 5, 2315.


Tostmann, C. The function of the ground enamel. *Keram. Rundschau*, 19, 5–6 (1911); *C. A.*, 5, 1670. The claim is reasserted that in ground enamels on cast iron the cobalt oxide is reduced to cobalt.


Vondrácek, R. The function of the ground enamel. *Sprechsaal*, 44, 115; *C. A.*, 5, 2163.


1912


VITREOUS ENAMELING


Landau, Kreidl, Heller and Co. Alkali containing clouding agent for white enamels. German Patent 283,792, Aug. 24, 1912. C. A., 10, 262. Metal compounds, other than those of tin, are used.

Landau, Kreidl, Heller and Co. Clouding agents for white enamels. English Patent 16,787, July 18, 1912. C. A., 8, 410. Zircon is partially dis-integrated by heating with sodium hydroxide or carbonate and the soluble silicates and surplus alkali removed with water. The combined alkali is partly removed by treating the mass with ammonium or metallic salts and the product then heated until the water of hydration is removed.


Landau, Kreidl, Heller and Co. White enamels. Swiss Patent 62,594, July 8, 1912. C. A., 8, 2236. Alkali containing hydroxides of the known metal compounds, used heretofore as obscuring agents, are here employed for that purpose.

Landau, Kreidl, Heller and Co. White enamels. English Patent 29,382, Dec. 20, 1912. C. A., 8, 2046. The amount of water of hydration contained in the hydrated oxide used as the opaquing agent is varied in inverse proportion to the per cent of alkali used.


Rickmann, R. Testing of enamels containing antimony. Z. angew. Chem., 25, 1518–19 (1912); J. Soc. Chem. Ind., 31, 775. The sample is boiled for half an hour with 4 per cent acetic acid or 2 per cent tartaric acid. The antimony in solution is titrated with permanganate. The meta-antimonates are not attacked by this treatment.


Rickmann, R. The use of antimony compounds for the production of white enamel. Sprechsaal, 45, 115–7 (1912); La Ceramique, 15, 134; C. A., 6, 1348, 2679; J. Soc. Chem. Ind., 31, 231. Antimony oxide should be avoided, but the antimonates are not injurious to health.


White enamel with zirconium silicate base. La Ceramique, 14, 204; C. A., 6, 1665. The natural silicate of zirconium, extracted with hydrochloric acid, and then with 4 parts of sodium hydroxide at 500–600 gives a product that is bulky and superior to tin oxide.


1913


Berge, A. Leadless enamels and faience with reduced content of tin oxide. Sprechsaal, 46, 17–9(1913); J. Soc. Chem. Ind., 32, 142. Instead of dispensing with tin oxide, it is reduced to a minimum by fritting with sodium phosphate.

Bertrand, M. S. V. Enamels of sodium borosilicate. La Ceramique, 16, 113–4; C. A., 7, 2841.

Davidson, T. R. Cleaning of metal articles preparatory to the application of a coating of enamel or the like. English Patent 16,554, July 18, 1913 J. Soc. Chem. Ind., 33, 355. Concentrated sulfuric acid is used to carbonize the grease, and the pieces are then allowed to stand in water, where the diluted acid further cleans the articles.


Deleuil, S. L. Enameling metal plates. French Patent 456,959, Apr. 22, 1913. C. A., 9, 137. The plates, after immersion in the bath, are freed from excess by rapid turning.

Eyer, Ph. The assumed reduction of antimonic to antimonous compounds in enamels. Glashütte, 43, 266, 327–8; C. A., 7, 3004. This does not take place.


Eyer, Ph. Quartz and clay in enameling. Glashütte, 43, 662–3; C. A., 7, 3647.


Importance of powdered coal in enamel works. Glasshütte, 43, 1004–6; C. A., 8, 1194. The relative value of 3 varieties of charcoal and coal are discussed.

Influence of sulfur dioxide used as a disinfectant upon sheet steel enamel. Keram. Rundschat, 21, 380; C. A., 8, 224. Dry or water-laden sulfur dioxide is without effect upon perfect ware, but on ware exhibiting crazing defects, yellow spots are formed in the defective spots of the enamel. If the ware itself is wet, however, the sulfur dioxide fumes exert vigorous effect, due to sulfuric acid formation.


Landau, Kreidl, Heller and Co. White enamels and opacifiers for white enamels. La Céramique, 16, 238-40; C. A., 8, 224. The opacifying effects of the metallic oxides are influenced by combinations with small amounts of phosphoric acid. Combining water of hydration and alkali or alkaline earths to the above phosphate further favorably influences the opacifying effect.

Landau, Kreidl, Heller and Co. White enamels of a zircon base. La Céramique, 16, 61-2; C. A., 7, 2671; La Céramique, 17, 52-3; C. A., 8, 2233.


Michel, R. Iridescent enamel. French Patent, Addition 17,326 to 455,064, Feb. 7, 1913. C. A., 8, 2046. Glass or enamel ware, immediately after production, is exposed at a suitable temperature to metal bromide vapors.


Removing enamels. Glashütte, 43, 326-7; C. A., 7, 3004. The use of sodium hydroxide at 180° with 12 atmospheres pressure is suggested.

Schuler, A. J. Process for dulling enamels. Canadian Patent 146,740, Mar. 18, 1913. C. A., 7, 1792. A silicious material is mixed with the covering mass and burned in a furnace on the article to be enameled.
Schuler, A. J. Roughening of enamels. *La Ceramique*, 16, 239-40; *C. A.*, 8, 224. Quartz, feldspar or kaolin is mixed with a cover compound of earths or silicates and salts before application to the object.


1914


Berge, A. Enamel glazes free from lead and tin. *Sprechsaal*, 47, 330-41; *C. A.*, 8, 3493; *J. Soc. Chem. Ind.*, 33, 647. Antimony compounds are used as a substitute for the more costly tin oxide in producing opacity. Formulas are given.


Don'ts relative to enameled iron ware. *Metal Work*, 82, 410-1 (Sept. 18, 1914).

Eyer, Ph. Use of sodium silicofluoride in enamel glazes and in the glass industry. *Glashütte*, 44, 205-7 (1914); *C. A.*, 8, 2468.


Kraze, F. The technic of iron enamels applied dry. *Sprechsaal*, 47, 535–8, 545–6 (1914); C. A., 9, 957.


Vondracek, R. Covering power of clouding agents for enamels. *Sprechsaal*, 47, 341–2; C. A., 8, 3493; *J. Soc. Chem. Ind.*, 33, 647. Water and alkali containing forms of the oxides of tin, zirconium and titanium are used. The increased covering properties are probably due to the oxides being in a state of a colloidal gel.


1915


Chem. Ind., 36, 879. Within a rather narrow limit in sizing, reasonable uniformity can be obtained in the loss in weight of a two-gram sample of frit ground to pass 20 mesh when exposed to a given solution.


Schwarzbach. A hint from enamel technology. Diamant, 37, 525–6; C. A., 10, 960. To secure uniform and complete fusion the addition of borax, magnesium oxide, or ammonium chloride is recommended.


1916


Black enamels. Schnurpfeil's Rev. Glass Works, 2, 137 (1916); C. A., 10, 2133. Five formulas are given.


Zinc sulfide as an opacifying agent. *Keram. Rundschau*, 24, 5, 29 (1916); *C. A.*, 11, 3106. Addition of not more than 5 per cent of zinc sulfide produces opaque enamels.

1917

Continuous enameling and stoving machine for small parts. *Engineering*, 103, 410 (1919); *C. A.*, 11, 2146.


Kretzer, H. Clouded enamels and glasses. Swiss Patent 73,471, May 1, 1917. *C. A.*, 11, 3406. Silicon compounds of acid character are added to the enamel mass after melting and while grinding.


Schaeffer, J. The use of zinc sulfide in white and luminous enamels. *Keram. Rundschau*, 25, 75; *C. A.*, 12, 2677; *J. Soc. Chem. Ind.*, 37, 584. In sheet steel enamels of suitable composition zinc sulfide is an excellent opacifier in the absence of metallic oxides which tend to decompose it. The opacity is equal to that produced by stannic oxide, but the enamels are not so white nor brilliant.


Verein Chem. Fabrik Landau. White enameling. Swedish Patent 41,858, Jan. 10, 1917. *C. A.*, 11, 1735. The clouding agent is an anhydrous zirconium compound, poor in alkali, which is treated with salts of metals whose hydroxides or oxides themselves produce clouding effects.
VITREOUS ENAMELING


1918


Dreissen, Cl. G. Enamels and ceramic pigments. Pol. Weekblad, 1918, Nos. 5, 6, 8; Chem. Weekblad, 16, 865-6; C. A., 13, 2115. Review.

Frost, Leon J. The action of acetic acid solutions of different strengths on a sheet steel enamel. J. Am. Ceram. Soc., 1, 422-8 (1918); C. A., 13, 175; J. Soc. Chem. Ind., 38, 107A. Twenty to 25 per cent acid is the most corrosive.


1919


Poste, E. P. Relative action of acids on enamels. II. J. Am. Ceram. Soc., 2, 32-43 (1919); C. A., 13, 1136; J. Soc. Chem. Ind., 38, 287A. Twenty per cent acid has the maximum effect. Citric and tartaric acids are more active than acetic acid.

Springer, L. What precautions should be taken in replacing soda or potash (in glasses and enamels). *Sprechsaal* 52, 362-3 (1919); *C. A.*, 14, 809; *J. Soc. Chem. Ind.*, 38, 902A.


1920

Landrum, Robert D., and Frost, Leon J. Titanium enamels. *J. Am. Ceram. Soc.*, 3, 316-21 (1920); *C. A.*, 14, 2688. The good qualities resulting from the use of titanium seem to more than offset the bad ones and it seems possible to overcome some of the difficulties and develop enamels of very substantial practical value.

Lindemann, W. C. The electric cleaning of metals for enameling purposes. *J. Am. Ceram. Soc.*, 3, 252-5 (1920). The electric cleaning process is superior to the older scaling or burning off method.


Shaw, J. B. Fish scaling. *J. Am. Ceram. Soc.*, 3, 489-97 (1920); *C. A.*, 14, 2689. Chemical composition has very little bearing on the subject of fish scaling. It is probably due to a number of contributory causes, which are discussed.
UNITED STATES PATENTS RELATING TO ENAMELS
WITH SPECIAL REFERENCE TO ENAMELS FOR
IRON AND STEEL

The following pages contain a list of the United States patents relative to enamels, with special reference to those for iron and steel for the period 1900–1920. These are arranged chronologically. Wherever possible reference is given to Chemical Abstracts, where a more complete abstract of the patent may usually be found. Reference is also made (the figures in parentheses), to the Official Gazette of the U. S. Patent Office, where the more important, if not all, the claims of the patents are printed. Printed copies of patents are furnished at 10 cents each by the Commissioner of Patents, Washington, D. C.


The formula used was: 61 parts borax, 71 parts feldspar, 44 parts quartz, 15 parts fluor spar, 14 parts soda, 11 parts saltpeter and water.


Variegated enamel ware, the surface of which comprises a body having incorporated and fused therein an enameling material of different color.


A thin finish coat is applied to a burned ground coat and while this is still wet, a second thin coat of a contrasting color is applied.
Iron or steel is coated with a suitable primary coating (alkali carbonate) and an enamel coat containing a suitable percentage of primary or acid salt capable of decomposing the film.
The cleaned article is coated with a thin layer of cohesive and non-corrosive metal and an enamel then applied which, upon heating, will coact with and only partially oxidize and permeate the coating metal.
The plates are coated with a mixture of zinc white and oil varnish, dried, then coated with a greasy lacquer color, dried and rubbed.
Sodium antimoniate is fused with the enamel.
The cleaned article is coated with an enamel carrying metallic bodies, a non-metallic hydroxide added and heated to flux and set the enamel.
Steel is pickled, washed, dried, immersed in an acid solution and coated while wet with alkaline liquid enamel, dried and fused.


The plate is coated with a preparation of enamel, burned, the plate then slushed in an enamel preparation and the enamel evenly distributed by a blast of air.


An iron or steel article which has a fundamental coat composed of clay and an oxidizing agent and a separately applied glaze coat covering the fundamental coat and forming therewith a mottled finish.


The process consists of mixing a comparatively small amount of comminuted carborundum with dry pulverized enamel material of one color (different from the carborundum), putting the mixture on the article to be coated with enamel, and then subjecting the article to such heat as fuses the enamel material but less than sufficient to fuse the carborundum.


After cleaning the metal is coated with an alkaline material, the enamel is then applied, a coloring coat applied and burned, and a second coat of enamel applied and burned.


The process consists in first forcibly beating one metal into and upon the other systematically and continuously until the particles or molecules of the coating metal are driven into the metal being coated and incorporated with the particles at and beneath the surface of the same.


A flux of white opal cullet 130, sodium bicarbonate 20, and boric acid 12 parts is ground in water to a fine powder, applied to the article and burned.


The article to be enameled is heated in a rotating enameling chamber or furnace containing dry enamel material.


The boiled, roasted and ground product of Sb oxide 70, NaOH 28, NaN0₃ 22, kaolin 10 and barytes 10.
A coating containing a magnetic material and sulfur is deposited upon the article electrolytically and the enamel is applied to this. 994,162. Edgar L. Hull. Producing flat watch dials, enameled on one side. June 6, 1910. C. A., 5, 2540. (167, 22).
Both sides are enameled and the enamel then removed from one side by the action of HF.
A glazing mass and a silicate of Zr, Th, Gl, La, or Yt.
Zirconium silicate and sodium hydroxide.
Heating a mixture of 2 per cent silver, 8 per cent copper and 8 per cent lead, melted together with 82 per cent sulfur and powdering the product.
Hydrated alkali zirconate, stannate, or titanate, combined with silica.
Immersed in conc. sulfuric acid at 90–150 degrees, then washed with water at 65 and then at 100 degrees.

Contains spinel and preferably small amounts of zirconium, titanium stannic or silicon oxide as opaquing material.

Contains colloidal zirconium oxide.

Natural zirconium silicate is heated with 4 times its weight of sodium hydroxide to 500–600 degrees, washed, dried, and heated to a glowing temperature.

The opaquing material is formed of zirconium oxide combined with silica and about 3–4 per cent of alkali metal.


Finely comminuted colored glass in addition to the ordinary enamel to form a speckled coating.


Hydrates zinc oxide containing 2–7 per cent combined alkali and a few per cent of water, varying inversely as the amount of alkali.

The opaquing agent consists of zirconium oxide combined with a small amount of alkali.


Hydrates stannic oxide containing about 10 per cent water and 3–5 per cent of alkali.
Alkaline compound of zirconium formed by treating with acid and washing to remove part of the combined alkali.

1,153,748. C. Baezner. Opaque enamel or glazing composition for use on sheet iron, etc. Sept. 14, 1915. C. A., 9, 3343. (218, 528).

The iron is immersed in a bath prepared from dilute sulfuric acid, ferric oxide and an enamel composition.

Neutralized anhydrous calcium stannate is used as an opaque coloring.


Small proportion of potassium antimoniate is added.

A mixture of various asphalts, rosin, Portland cement, etc., is used.

A mixture of titanium oxide and zirconium oxide is used for opaquing white enamels.


The opacifying agent, e. g., a compound of Zr, Ti, Si, Al, Zn, or alkaline earth metal, is added to the other ingredients of the enamel after they have been at least partially ground in a wet mill, together with substances which precipitate colloids, such as ammonium chloride, magnesium sulfate, or chloride, or sodium sulfate.

Ore containing cobaltic oxide, freed from sulfur and arsenic, is used to color the enamel.

White enamel for glass consisting of ruby glass, clay, cryolite and sodium carbonate.


Treated first with HCl (10 per cent) at 70 degrees and then with 25 per cent NaOH at 70 degrees.


A plurality of contracting members for engaging the rims of articles to be enamelled attached to a rotating shaft.


The furnace is adapted to melting enamels in crucibles.


Relatively low content of the usual opacifying agents, such as tin or zinc oxide is used by suitable mixing with other auxiliary ingredients.


Zirconium borate supersaturated with zinc oxide is used as a clouding material in enamels.


Sheet steel is coated with oil and subjected to a drawing operation, the ware then is heated to remove the oil which produces a thin oxide coating on the metal, the enamel is then applied and baked.


Triple silicate of Al, Na, and Ca mixed with fluorides and coloring substances.
