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METHOD FOR ELECTROLYTICALLY POLISHING STAINLESS STEEL

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ABSTRACT OF THE DISCLOSURE

Method for electrolytically polishing stainless steel to effect a pear-like appearance thereon which comprises electrolyzing a solution consisting essentially of water, sulfuric acid and an effective amount of an additive which sticks unevenly on the surface of the stainless steel anode during electrolysis. Additives which may be employed include high molecular weight substances such as starch, glue, sawdust and paper, sugars such as dextrose and mannitol, organic acids or salts thereof such as malic acid, citric acid, succinic acid, tartaric acid, acetic acid, gluconic acid, sodium malate and sodium gluconate, polyhydric alcohols such as glycerine, ethylene glycol and inositol, amines such as butylamine and 2-ethylhexylamine, picoline, nicotinic acid amide, synthetic high molecular weight substances such as polyvinyl alcohol and polyethylene glycol and amino acids such as aspartic acid, glutamic acid and glycine. Electrolysis is carried out at a temperature of from 0° to 100° C. and at a current density of from 5 to 500 amperes per square decimeter.

This invention relates to an electrolytic polishing solution for effecting pear-like appearance on a stainless steel surface which comprises an aqueous solution containing 0.5–100 moles/kg. water of sulfuric acid to which one or more of substances are added, which are capable of unevenly sticking solid, viscous liquid or bubbles on the surface of the anode of stainless steel.

The term "pear-like appearance surface" used in this specification means a surface similar to pear skin or an uneven surface, and it is to be construed in somewhat broader sense including coarsely uneven and finely uneven surface with or without lustre.

In the prior art for polishing stainless steel surface to give pear-like appearance, such methods as blasting of particles of sand, Carborundum, Alundum, etc., onto the surface have been employed. However, the operations according to these methods are unsanitary because of much dusts.

Furthermore, the pear-like appearance surface obtained by said prior art methods has usually unsatisfactory lustre. When a lustrous surface is desired, the surface must be further electrolytically polished.

An electrolytic polishing method for obtaining a lustrous mirror-like surface of stainless steel have been industrially carried out. However, flaws given on the lustrous mirror-like surface are conspicuous, while those on the pear-like surface are not.

The present inventors conducted research on the method for electrolytically polishing stainless steel surface to give

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pear-like appearance thereon, and found that the surface of stainless steel is polished to give pear-like appearance, when the electrolytic polishing of stainless steel is carried out using electrolytic solution comprising an aqueous solution containing 0.5–100 moles/kg. water of sulfuric acid to which one or more of substances are added, which are capable of unevenly sticking solid, viscous liquid or bubbles on the anode of stainless steel to be polished.

The examples of said substances are as follows: high molecular substance produced from animals or plants (e.g. starch, glue, sawdust, paper, etc.) sugars (e.g. sugar, dextrose, mannitol, etc.), organic acids or salts thereof (e.g. malic acid, citric acid, succinic acid, tartaric acid, acetic acid, gluconic acid, sodium malate, sodium gluconate, etc.), polyhydric alcohol (e.g. glycerine, ethylene glycol, inositol, etc.), amines (e.g. butyl amine, 2-ethylhexylamine, etc.), picoline, nicotinic acid amide, synthetic high molecular substances (e.g. polyvinyl alcohol, polyethylene glycol, etc.), amino acids (e.g. aspartic acid, glutamic acid, glycine, etc.). The surface of stainless steel can be polished to give pear-like appearance by carrying out electrolysis using the stainless steel as anode and said aqueous sulfuric acid solution containing one or more of said substances as the electrolyte.

The concentration range of sulfuric acid in the electrolyte is 0.5–100 moles/kg. water to give a desirable pear-like appearance. However, the optimum range is 0.5–45 moles/kg. water.

The effect of addition of said substances to the aqueous sulfuric acid solution is as follows: By the addition, one or more kinds of solid, viscous liquid and bubbles are stuck on the surface of anode during electrolysis. Thus the current is interrupted. Since the degrees of the interruption are partly different, the dissolution of the surface becomes uneven and thus a pear-like appearance is produced. The amount of said additive is not especially critical, but 1–1500 g./kg. water is preferable. The temperature range of the electrolyte for a pear-like appearance is 0°–100° C. As the temperature rises, the conductivity of the electrolyte becomes higher and the necessary electrolytic voltage falls, and furthermore the drag-out becomes small. The optimum temperature range for a lustrous pear-like surface is 60°–90° C. When the temperature is lower than 50° C., a fine pear-like surface is obtained and when higher than 90° C., carbonization of the additive vigorously takes place and the polished surface becomes uneven.

The anodic current density range for producing pear-like surface is broad, that is, 5–500 a./dm.² and preferably 7–200 a./dm.². When the current density is low, the surface becomes non-lustrous and when it is high, residual strip or non-uniform lustre is produced on the surface.

The time required for the electrolytic polishing is usually less than five minutes to give a pear-like appearance and 3–4 minutes are practically suitable.

Regarding the quality of stainless steel to be electrolytically polished, more lustrous and beautiful pear-like surface is produced with the high class stainless steel (A.I.S.I. type series 3xx) than with the low class stainless steel (A.I.S.I. type series 4xx). For example, when 13 chromium steel is electrolytically polished using a bath of aqueous sulfuric acid solution to which said additive is added under the same conditions as those under which

18-8 stainless steel electrolytically polished to give a lustrous pear-like surface, a lusterless pear-like surface is produced in most cases. However, a lustrous pear-like surface of 13 chromium steel is obtained by using an electrolyte mainly composed of aqueous sulfuric acid solution to while a small amount of phosphoric acid is added.

The relation between the concentration of sulfuric acid and the amount of the additive is as follows: When the concentration of sulfuric acid is high, e.g. 24-41 moles/kg. water, the small amount of the additive, e.g. 0.5-20 weight percent suffices to produce a pear-like surface. However, when the concentration of sulfuric acid is low, it is necessary to employ a large amount of additive and a high current density.

The relation between the concentration of sulfuric acid and the pear-like surface depends upon other conditions. However, when the sulfuric acid concentration is, for example, 12-58 moles/kg. water, relatively coarse pear-

like surface is obtained and when outside said range, relatively fine pear-like surface is obtained.

With 18-8 stainless steel, when the stuck matters exist on the whole surface, relatively coarse good pear-like surface is obtained, while when the stuck matters are not found, usually a fine pear-like surface is obtained.

Said stuck matters are solid, viscous liquid or a mixture thereof which can be removed by washing it with water to dissolve therein.

With 13 chromium steel, the stuck matters are thin or hardly found. However, the generated bubbles are stuck on the surface to give a pear-like surface.

The mechanism of formation of the pear-like surface is not yet known. However, it seems that during the electrolysis one or more of solid, liquid and bubble are stuck on the surface and due to the partial differences of the sticking condition, thickness or concentration, the pear-like surface is produced.

The following examples will illustrate this invention.

Run No.						
	1	2	3	4	5	6
Composition of electrolyte (part by weight):						
Sulfuric acid	73	80	65	70	55	75
Phosphoric acid	0	0	0	0	0	0
Water	27	20	35	30	45	25
Additive	Mannitol 1	Starch 1	Sugar 2	Filter paper 1	Malic acid 10	Citric acid 1
Temperature of electrolyte (° C.)	75	80	85	70	80	70
Electrolytic voltage (v.)	4-6	5-7	6-7	6-8	6-7	5-6
Current density (a./dm. ²)	10	15	15	15	18	15
Time of electrolysis (min.)	4	4	4	4	5	5
Kind of steel						
	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel
Result of polishing:						
Pear-like surface (unevenness)	Good	Good but a little fine	Good	Good	Good but a little fine	Good
Degree of uniformity	Uniform With a little lustre.	Uniform With lustre	Uniform With lustre	Almost uniform With semilustre	Uniform With lustre	Uniform With lustre
Run No.						
	7	8	9	10	11	12
Composition of electrolyte (part by weight):						
Sulfuric acid	70	65	70	70	60	70
Phosphoric acid	0	0	0	0	0	0
Water	30	35	30	30	40	30
Additive	Succinic acid 0.5	Sodium tartarate 0.5	Glycerine 1	Ethylene glycol 2	Butyl amine 1	2-ethylhexyl amine 1
Temperature of electrolyte (° C.)	70	75	70	75	70	80
Electrolytic voltage (v.)	5-6	5-7	6-7	6-7	5-7	4-6
Current density (a./dm. ²)	15	15	17	15	15	15
Time of electrolysis (min.)	4	5	2	5	5	4
Kind of steel						
	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel
Result of polishing:						
Pear-like surface (unevenness)	Good	Good	Good but a little fine	Good	Good	Good
Degree of uniformity	Almost uniform	Almost uniform	Almost uniform	Almost uniform	Uniform	Almost uniform
Lustre	With semilustre	With semilustre	With semilustre	With lustre	With lustre	With lustre
Run No.						
	13	14	15	16	17	18
Composition of electrolyte (part by weight):						
Sulfuric acid	60	75	65	73	75	70
Phosphoric acid	0	0	0	0	0	0
Water	40	25	35	27	25	30
Additive	10	Polyvinyl alcohol 1	Polyethylene glycol 2	Aspartic acid 1	Acetic acid 1	Glutamic acid 0.5
Temperature of electrolyte (° C.)	80	75	70	75	70	70
Electrolytic voltage (v.)	4-6	5-8	7-9	5-7	4-6	5-7
Current density (a./dm. ²)	15	15	15	15	15	15
Time of electrolysis (min.)	4	5	5	5	5	5
Kind of steel						
	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel
Result of polishing:						
Pear-like surface (unevenness)	Good but a little fine	Good	Good	Good	Good	Not so good
Degree of uniformity	Uniform	Uniform	Uniform	Almost uniform	Almost uniform	Non uniform
Lustre	With lustre	With lustre	With lustre	With semi-lustre	Without lustre	Without lustre

	Run No.					
	19	20	21	22	23	24
Composition of electrolyte (part by weight):						
Sulfuric acid.....	75.....	75.....	61.....	70.....	65.....	65.....
Phosphoric acid.....	0.....	0.....	0.....	5.....	7.....	0.....
Water.....	25.....	25.....	39.....	25.....	28.....	35.....
Additive.....	Sodium gluconate 1.....	Saw dust 1.....	Malic acid 6.....	Sodium malate 5.....	Malic acid 2.....	Mannitol 3.....
Temperature of electrolyte (° C.).....	73.....	70.....	80.....	75.....	70.....	70.....
Electrolytic voltage (v.).....	5-7.....	5-8.....	4-6.....	5-7.....	5-7.....	5-7.....
Current density (a./dm. ²).....	15.....	17.....	15-20.....	15-20.....	15-20.....	15-20.....
Time of electrolysis (min.).....	4.....	4.....	5.....	5.....	4.....	5.....
Kind of steel						
	18-8 stainless steel	18-8 stainless steel	13 chromium steel	13 chromium steel	13 chromium steel	13 chromium steel
Result of polishing:						
Pear-like surface (unevenness).....	Good.....	Good.....	Good but a little fine.....	Good but a little fine.....	Good but a little fine.....	Good but a little fine.....
Degree of uniformity.....	Uniform.....	Almost uniform.....	Uniform.....	Uniform.....	Uniform.....	Uniform.....
Lustre.....	With lustre.....	With a little lustre.....	With a little white.....	With lustre.....	With lustre.....	With a little white.....

	Run No.					
	25	26	27	28	29	30
Composition of electrolyte (part by weight):						
Sulfuric acid.....	73.....	73.....	75.....	73.....	49.....	980.....
Phosphoric acid.....	0.....	0.....	0.....	0.....	0.....	0.....
Water.....	27.....	27.....	25.....	27.....	1,000.....	1,000.....
Additive.....	Sodium gluconate 0.5, malic acid 0.5.....	Sodium gluconate 0.5, mannitol 0.5.....	Malic acid 0.5, mannitol 0.5.....	Picoline 0.5, malic acid 0.5.....	Mannitol 1,400.....	Starch 500.....
Temperature of electrolyte (° C.).....	75.....	80.....	78.....	80.....	75-85.....	75-85.....
Electrolytic voltage (v.).....	6-7.....	5-7.....	5-7.....	4-6.....	4-5.....	5-7.....
Current density (a./dm. ²).....	15.....	15.....	15.....	15.....	100.....	200.....
Time of electrolysis (min.).....	4.....	4.....	4.....	4.....	4.....	4.....
Kind of steel						
	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel
Result of polishing:						
Pear-like surface (unevenness).....	Good.....	Good.....	Good.....	Good.....	Fine.....	Good.....
Degree of uniformity.....	Uniform.....	Uniform.....	Uniform.....	Uniform.....	Uniform.....	Uniform.....
Lustre.....	With lustre.....	With lustre.....	With lustre.....	With lustre.....	Dull.....	With lustre.....

	Run No.					
	31	32	33	34	35	36
Composition of electrolyte (part by weight):						
Sulfuric acid.....	490.....	980.....	49.....	500.....	800.....	900.....
Phosphoric acid.....	0.....	0.....	0.....	0.....	0.....	0.....
Water.....	1,000.....	1,000.....	1,000.....	1,000.....	1,000.....	1,000.....
Additive.....	Malic acid 800.....	Glycerine 300.....	Picoline 1,700.....	Saw dust 700.....	Butyl amine 500.....	Glutamic acid 250.....
Temperature of electrolyte (° C.).....	70-80.....	75-80.....	65-70.....	73-80.....	72-82.....	68-80.....
Electrolytic voltage (v.).....	5-6.....	5-7.....	5-6.....	5-6.....	5-6.....	4-5.....
Current density (a./dm. ²).....	150.....	200.....	80.....	120.....	85.....	38.....
Time of electrolysis (min.).....	5.....	4.....	6.....	5.....	5.....	4.....
Kind of steel						
	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel	18-8 stainless steel
Result of polishing:						
Pear-like surface (unevenness).....	A little fine.....	Good.....	Very fine.....	Coarse.....	Almost good.....	Coarse and partially fine.....
Degree of uniformity.....	Almost uniform.....	Almost uniform.....	Almost uniform.....	Uniform.....	Almost uniform.....	Almost uniform.....
Lustre.....	With a little lustre.....	With lustre.....	Dull.....	With a little lustre.....	Dull.....	Irregular.....

	Run No.		
	37	38	39
Composition of electrolyte (part by weight):			
Sulfuric acid.....	800.....	980.....	900.....
Phosphoric acid.....	0.....	300.....	0.....
Water.....	1,000.....	1,000.....	1,000.....
Additive.....	Polyvinyl alcohol 320.....	Malic acid 1,700.....	Nicotinic acid amide 980.....
Temperature of electrolyte (° C.).....	72-87.....	70-80.....	70-80.....
Electrolytic voltage (v.).....	5-6.....	5-7.....	5-7.....
Current density (a./dm. ²).....	158.....	38.....	200.....
Time of electrolysis (min.).....	4.....	5.....	5.....
Kind of steel			
	18-8 stainless steel	13-chromium steel	18-8 stainless steel
Result of polishing:			
Pear-like surface (unevenness).....	Very fine.....	Fine.....	Good.....
Degree of uniformity.....	Almost uniform.....	Uniform.....	Uniform.....
Lustre.....	With a little lustre.....	With a little lustre.....	With lustre.....

What we claim is:

1. A method for electrolytically polishing stainless steel to effect a pear-like appearance thereon which comprises electrolyzing a solution consisting essentially of water, sulfuric acid in an amounts of 0.5-100 moles/kg. of water and an effective amount of an additive selected from the group consisting of sawdust, dextrose, mannitol, malic acid, succine acid, tartaric acid, sodium malate, ethylene glycol, inositol, butylamine, 2-ethylhexylamine, picoline, nicotinic acid amide, polyethylene glycol, aspartic acid, glutamic acid and mixtures thereof at a temperature of from 0° to 100° C. and a current density of from 5 to 500 amperes per square decimeter, the metal to be polished constituting the anode, until the desired pear-like appearance is attained.
2. The method of claim 1, wherein the amount of additive employed is 1-1500 g./kg. of water.
3. The method of claim 1, wherein said solution also contains a small amount of phosphoric acid.
4. The method of claim 1, wherein the current density during the electrolysis is from 7 to 200 amperes per square decimeter.
5. The method of claim 4, wherein the electrolysis is carried out at temperature of from 60° to 90° C.
6. The method of claim 5, wherein the amount of additive employed is 1-1500 g./kg. of water.
7. The method of claim 6, wherein the additive is sawdust.
8. The method of claim 6, wherein the additive is

selected from the group consisting of dextrose and mannitol.

9. The method of claim 6, wherein the additive is selected from the group consisting of malic acid, succinic acid, tartaric acid and sodium malate.

10. The method of claim 6, wherein the additive is selected from the group consisting of ethylene glycol and inositol.

11. The method of claim 6, wherein the additive is selected from the group consisting of butylamine and 2-ethylhexylamine.

12. The method of claim 6, wherein the additive is picoline.

13. The method of claim 6, wherein the additive is nicotinic acid amide.

14. The method of claim 6, wherein the additive is polyethylene glycol.

15. The method of claim 6, wherein the additive is selected from the group consisting of aspartic acid and glutamic acid.

16. The method of claim 6, wherein electrolysis is carried out for from 2 to 6 minutes.

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