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(12) # EUROPEAN PATENT APPLICATION

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(54) **Anti-corrosion treatment process for iron materials.**

(57) A novel anti-corrosion treatment process for iron materials is disclosed. The treatment comprises forming zinc coating on the surface of an iron material by the mechanical zinc plating and then treating the plated surface with a non-aqueous chromating composition. The process brings about practically sufficient anti-corrosion effect economically without provision for treating waste liquid.

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Title of the Invention

Anti-corrosion treatment process for iron materials

Field of the Invention

This invention relates to an anti-corrosion treatment process for iron materials (iron and iron alloys). More particularly, this invention relates to an anti-corrosion treatment process for iron materials comprising forming a zinc coating on the surface of an iron material and thereafter treating the coated surface with a non-aqueous chromating treatment composition.

Background of the Invention

It is well-known to coat the surface of steel materials with zinc by hot-dip plating or electrolytic plating. Rather recently, a method of coating an iron material with zinc has been developed, said method comprising projecting onto the surface of said material a blast material comprising an aggregation of particles each comprised of an iron core and a zinc crust surrounding the iron core with intermediate layers of iron-zinc alloys (Japanese Laid-Open Patent Publication No. 45372/81). This is an improved version of the so-called mechanical plating, which has been known since around 1965 as disclosed in British Patent No. 1,041,620.

The method of Japanese Laid-Open Patent Publication No. 45372/81 comprises projecting onto the surface of an iron material a blast material which is an aggregation of independent particles comprised of a core substantially of iron a crust substantially of zinc which is formed on the surface of the core particle with iron-zinc alloy layers between the core and the crust. Here "substantially of iron", means the core is pure iron or iron alloy containing a small amount of silicon, manganese, chromium, nickel, etc. and "substantially of zinc" means pure zinc or zinc alloy containing a small amount of copper, aluminum, magnesium, silicon, tin, etc. The intermediate iron-zinc layers

are a plurality of layers of different Fe-Zn intermetallic compounds.

The zinc blast material can be prepared by melt coating or diffusion coating. The proportion of iron and zinc in the blast material is 10 - 95 % by weight of iron to 5 - 90 % by weight of zinc, preferably 10 - 70 % by weight of iron to 90 - 30 % by weight of zinc, more preferably, 15 - 65 % by weight of iron to 85 - 35 % by weight of zinc. A suitable proportion in this range is selected in accordance with the intended use. The particle size is generally under 16 mesh. Blasting can be effected using blast machines of various types including tumbler type, barrel type, etc.

The mechanical plating method is advantageous in that equipment cost and energy consumption are low and the environmental pollution factors are much limited. Although the method and material of said Japanese Patent Publication have radically overcome the defects of earlier mechanical plating, zinc-coating formed by this method is still insufficient in corrosion resistance and red rust is generated on an iron material coated with zinc at 100 mg/dm^2 by this method within 24 hours in the salt spray test. It is considered that this is because the formed coating film is of an iron-zinc alloy and is porous.

Therefore, even by the above-mentioned improved mechanical plating method (hereinafter referred to as "blast zinc plating") sufficient corrosion resistance cannot be expected unless it is used in combination with some other suitable method.

A rather simple anti-corrosion measure is the chromating process, of which there are three types of the baking chromating process, aqueous chromating process and non-aqueous chromating process.

The baking chromating process comprises coating a surface to be treated with a composition comprising a water-soluble chromic acid compound, a reducing agent and water, and baking the coated material to

reduce the chromic acid compound so as to form a water-insoluble chromate coating film. "Hynack" of Pennwalt Company, "Dacromet 100" of Diamond Shamrock Company, etc. are well known agents for the process of this type. The formation of a coating film in the baking chromating process is based on reduction of the chromic acid on heating in the presence of a reducing agent, and therefore, the reduction of the chromic acid is effected without fail, even if the substrate is an iron-zinc alloy coating formed by the blast zinc plating. However, such treatment is disadvantageous in that a step for removing excessive treating agent adhering to the substrate being treated and steps for drying and baking the green substrate are required and thus it requires higher equipment cost, more extensive plant space, increased number of the process steps, and increased consumption of energy, and as a result the production cost is higher.

The aqueous chromating process comprises treating the surface of a galvanized steel material with a mixture of a water-soluble chromic acid compound, a strong acid and water. This is an age-old well known technique disclosed in several text books such as "Mekki Gijutu Binran" published by Nikkan Kogyo Sinbunsha, etc. The aqueous chromating treatment is effective for pure zinc, but is not so effective for iron-zinc materials as for pure zinc, since the formed film is considerably irregular. The aqueous chromating composition is a mixture of water, a water-soluble chromic acid compound and a strong acid such as sulfuric acid, the zinc reacts with the strong acid on the surface being treated to produce nascent hydrogen, which reduces the chromic acid to form a chromate film on the surface. The reaction takes place at the zinc-plated surface and therefore, a thick film cannot be easily formed. Also the aqueous chromating solution produces waste liquid containing a large amount of chromic acid and thus the cost of

the equipment required for waste liquid disposal and the operation therefor is huge. Therefore, it is not suitable to combine this process with the blast zinc plating, which is free from the problem of disposition of waste liquid.

The composition used in the non-aqueous chromating process essentially consists of a chromic acid compound, an organic solvent (usually halogenated hydrocarbon) and an alcohol as a solubilizer, and it may contain a stabilizer and a reaction promotor for formation of chromate film and they are disclosed in Japanese Patent Publication No. 5288/65 (Du Pont), Japanese Patent Publication No. 3363/67 (Du Pont), Japanese Laid-Open Patent Publication No. 62970/81 (Tokuyama Soda), Japanese Laid-Open Patent Publication No. 97476/80 (Nippon Paint) and Japanese Laid-Open Patent Publication No. 139679/81 (Nippon Paint). Rather recently, a very stable non-aqueous chromating treatment composition containing chlorofluorocarbon as the solvent was invented (copending Patent Application No.).

In the process of this invention, any non-aqueous chromating treatment composition can be used, but it will be advantageous to use a composition in which a chloroflurocarbon solvent is used.

We studied various chromating processes to be combined with blast zinc plating and found that a combination with the non-aqueous chromating treatment exhibits the best corrosion prevention effect and completed this invention.

Summary of the Invention

This invention provides a process for treating the surface of iron materials comprising forming a zinc coating layer on the surface of an iron material by projecting a blast material which is an aggregation of particles each comprising a core comprising substantially iron, intermediate layers of iron-zinc alloys and an outer crust substantially comprising

zinc; and treating the thus zinc-coated surface with a non-aqueous chromating composition comprising a chromic acid compound, halogenated hydrocarbon solvent, an alcohol solubilizer.

The process of this invention compensates for the insufficiency in the corrosion prevention effect of blast zinc plating without impairing its advantage.

Specific Description of the Invention

The blast zinc plating employed in this invention is described in detail in the above-mentioned Japanese Laid-Open Patent Publication No. 45372/81. However, an outline of the pertinent portions thereof is set out in the following.

The iron particles for the cores of the blast material of this invention can be manufactured by any known method such as the carbon reduction process, gas reduction process, atomizing method, mechanical pulverization process, etc. It is desirable to modify the shape and properties thereof by cold working and/or heat treatment in accordance with the treatments which the particles have undergone. That is to say, the particles should be made as round as possible, the surface layer is hardened by cold working, so as to obtain iron particles having excellent abrasion resistance and impact resistance. Further, the toughness of the iron particles can preferably be improved by alloying some of the above-mentioned elements. Such improvement in the toughness of the core iron particles contributes to prevention of fracture of the blast material having zinc crust, although fracture of the blast material is not practically observed.

Metallic zinc is rather brittle. Therefore, it is preferred that the zinc for forming the zinc crust of the blast material contains 3 - 5 % aluminum and/or 0.2 - 1 % copper. The impact resistance of the blast material is improved by alloying such elements. The blast material having an alloy crust

is prepared by the melt coating process.

The blast material having a neat zinc crust can also be prepared by the diffusion process. The diffusion process comprises heating a mixture of iron particles and zinc powder. Specifically, neat iron or alloyed iron particles are mixed with zinc powder, preferably further with 0.5 - 3 % on the basis of the metals of ammonium halide, preferably chloride added, in a container of iron or silicon carbide, at a temperature in the range of 400 - 700°C for 3 - 20 minutes so as to form zinc-iron alloy layers and a zinc crust around the iron cores. This process can be carried out by a batch-wise or continuously. When it is continuously carried out by feeding iron powder into an auger type or a pusher type externally heated furnace. The resulting material is made into zinc-crusted iron particles by simple crushing treatment. The thus obtained blast material is substantially the same as obtained by the melt coating process.

The organic solvent used in the non-aqueous chromating treatment is a halogenated hydrocarbon (this term encompasses chlorofluerocarbon) having 1 - 2 carbon atoms and chlorine and/or fluorine atoms as well as possible remaining hydrogens. That is, methylene chloride, chloroform, carbon tetrachloride, trichloroethane, trichloroethylene, perchloroethylene, trichlorotrifluoroethane, trichloromonofluoromethane, dichlorotetrafluoroethane, tetrachlorodifluoroethane, etc. and mixtures thereof can be suitably used. The factors to be considered in selecting solvent is that the solvent is homogeneously miscible with other components of the composition, it is in the liquid state at the temperature at which the chromating reaction proceeds at a significant reaction rate, etc. Chromic acid used in this invention is what is called chromic acid anhydride or chromium trioxide having a chemical formula CrO_3. Said chromic acid

anhydride is used in an amount of 0.01 - 10 parts preferably 0.1 - 8 parts, more preferably 0.2 - 5 parts by weight hereinafter referred to simply as parts per 100 parts of the halogenated hydrocarbon solvent. With an amount less than 0.01 part, the chromating reaction proceeds very slowly and with the amount in excess of 10 parts, decomposition of the used halogenated hydrocarbon solvent and solubilizer is accelerated and invites formation of incomplete coating and abatement of anti-corrosion effect.

The solubilizer used in this invention is a secondary or tertiary alcohol having 3 - 20 carbon atoms which is soluble in said halogenated hydrocarbon solvent. Generally, secondary propanol, tertiary butanol, tertiary amyl alcohol, triphenyl carbinol, etc. can be suitably used. Tertiary butanol (hereinafter referred to as t-butanol) is most suitable because it dissolves homogeneously in most of the compositions of this invention, is stable over a long period and is inexpensive. At least 1 part of the solubilizer per 100 parts of the halogenated hydrocarbon solvent is required, and 20 parts or larger amount can be used. As an increased amount of the solubilizer is used, an increased amount of chromic acid anhydride can be dissolved. With less than 1 part of the solubilizer, solubilization in not sufficient. More than 20 parts thereof can be used, but it may make the composition inflammable according to the use condition. Therefore up to 20 parts will be preferably used. The more preferred range is 2 - 10 parts.

The stabilizer used in this invention can be selected from a wide range of known compounds such as amines, quinones, nitro-, azo-, azoxyaromatic compounds, thiourea, dienes, organic nitrite salt, zinc fluoride, zinc oxide, etc. The stabilizer is unnecessary when chlorofluorocarbon is used as the

solvent, and therefore, chlorofluorocarbon is preferred. Examples of the stabilizer are: N-nitrodiphenylamine, azoxybenzene, hydroquinone, diisobutylamine, pentadiene, amyl nitrite, etc. These compounds can be used singly or in combination, and are used in an amount 0.001 - 5 parts per 100 parts of the halogenated hydrocarbon solvent. Outside of this range, little or no effect is expected or no correspondingly better effect is expected. The preferred range is 0.05 - 3 parts and the more preferred range is 0.1 - 2 parts.

The reaction promotor used in the process of this invention is hydrogen fluoride, an organic acid, water, etc. This component is not essential and can be omitted from the composition depending upon the condition. An organic acid having 1 - 20 carbon atoms can be used. Preferably an organic acid having a general formula $R-(COOH)_n$, wherein R is may be a straight-chained, branched or cyclic hydrocarbyl group, and may be substituted, and n is an integer of 1 - 3. Examples of these organic acid are: formic acid, acetic acid, lactic acid, stearic acid, oxalic acid, fumaric acid, maleic acid, malic acid, etc. and mixtures of thereof. These reaction promotors can suitably be used in an amount 0.001 - 10 parts, preferably 0.003 - 1 part, and more preferably 0.005 - 0.5 part per 100 parts of the halogenated hydrocarbon solvent, and hydrogen fluoride and organic acids are preferably in an amount of not more than preferably 0.12 part, Water should preferably be used within the limit that it dissolves homogeneously in the system. Under the lower limit, the effect as a reaction promotor is not expected, and above the upper limit, corrosion effect thereof on the materials or articles to be treated and the apparatus becomes manifested or the homogenity of the system, is impaired. The preferred content of the reaction promotor is 0.005 - 0.12 part.

The chromating treatment composition used in the process of this invention is substantially non-

aqueous, and the halogenated hydrocarbon solvent acts as a degreaser as well as makes the system non-flammable; the solubilizer renders all the ingredients to dissolve homogeneously in the system. It is essential that all the ingredients dissolve homogeneously in the system. If not, the resulting coating is non-uniform and does not bring about satisfactory anti-corrosion effect.

The procedure of the chromating treatment is as follows. The chromating treatment composition is kept at a temperature between 5°C and the boiling point and metal articles to be treated are contacted therewith for 1 second - 60 minutes, preferably for 30 seconds to 5 minutes. Thereafter, the metal surface is dried. When the temperature of the composition is lower than 5°C, the chromating reaction does not substantially proceed; and when the contact time is shorter than 1 second, substantially effective coating is not obtained; and when it is longer 60 minutes, non-uniform coating is sometimes formed which is not desirable because of poor appearance. Iron materials to be treated should preferably be degreased beforehand. However, not too large amount of oils on the surface thereof can be removed during the chromating treatment.

It is of course possible to improve the anti-corrosion performance by heating or irradiating ultraviolet rays after the treatment.

As has been described above, the process of this invention is substantially non-aqueous all through the process, and no measures for waste liquid disposal are required. Thus excellent anti-corrosion coating can be formed very economically.

When the product obtained by the process of this invention (I), those obtained by the hot-dip zinc plating process (II) and the product obtained by treating hot-dip zinc-plated material by the non-aqueous chromating treatment composition (III) are compared, product (III) is best in corrosion resistance,

product (I) comes second and product (II) is inferior. But the cost for preparing product (III) is three times that of (I). Corrosion resistance of product (II) is sufficient for ordinary uses. Thus it can be said that product (III) is of excessively superior quality.

Specific Description of Embodiments of the Invention

Now the invention will be explained in detail by way of working examples and comparative examples. However, the invention is by no means limited to such working examples.

Example 1 (melt coating of iron particles)

Iron particles smaller than 16 mesh were filled in a cylindrical container of silicon carbide, and annealed using a tunnel kiln furnace at 920°C with a residence time of 6 hours. The lump taken out was crushed and 16 - 32 mesh, 32 - 48 mesh, 48 - 60 mesh and 60 - 80 mesh fraction were collected.

The particle fractions were mixed with a molten zinc alloy (4 % aluminum, 0.5 % copper and the balance zinc) kept at 620 ±5°C under the condition indicated in Table 1. The mixture was cooled in the atmosphere, crushed with a hammer mill and finally pulverized with a impact type high speed pulverizer and screened. The properties of the obtained blast materials are indicated in Table 2.

Table 1

Particle Size	Fe (%)	Zn (%)	Reaction Temp. (°C)	Reaction Time (min.)
16 - 32	62±1	38±1	485±5	4 - 7
32 - 48	61±1	39±1	485±5	4 - 7
48 - 60	57±1	43±1	485±5	4 - 5
60 - 80	55±1	45±1	485±5	4 - 5

Table 2

Particle Size	Fe (%) in Blast Material	Zn (%) in Blast Material	Apparent Density (g/cm^2)	Hardness (Hv)
16 - 32	75 - 80	20 - 25	3.8 - 4.2	400 - 450
32 - 48	74 - 78	22 - 26	3.6 - 4.0	350 - 400
48 - 60	72 - 75	25 - 28	3.5 - 3.9	300 - 350
60 - 80	70 - 73	27 - 30	3.2 - 3.6	300 - 350

Example 2 (diffusion coating of iron particles)

The same iron particles as used in Example 1 were mixed with zinc powder in proportions indicated in Table 3, and further 0.6 % on the basis of the weight of the metals of ammonium chloride was added and mixed for the purpose of removing oxide film of the zinc powder. The mixture was filled in a cylindrical container of iron and placed in a heating furnace heated at 650°C, by which a reaction temperature of 550°C was rapidly achieved in the container, and the container was kept in the furnace for five minutes. Thereafter the container was cooled in the atmosphere and the resulting crusted particles were taken out. In this case, although zinc is heated higher than its melting point, iron particles and zinc do not coagulate prevented by the oxide film existing on the surface of the zinc powder. Therefore, no crushing is required.

Table 3

Particle Size	Fe (%)	Zn (%)	Reaction Temp. (°C)	Reaction Time (min.)
16 - 32	70±2	30±2	550	5 - 10
32 - 48	70±2	30±2	550	5 - 10
48 - 60	65±2	35±2	550	5 - 10
60 - 80	60±2	40±2	550	5 - 10

Chromating and Test Methods:

Hexagonal head mild steel bolts 10 mm x 40 mm in size were degreased with trichloroethane vapor, and thereafter the bolts were subjected to projection of 32 - 48 mesh iron-zinc blast material obtained by Example 1 for 30 minutes so that the surface of them was coated with iron-zinc alloy with a coating weight

of 100 mg/dm^2. The thus obtained iron-zinc-coated bolts were treated with the above described non-aqueous chromating treatment composition. Each 5 pieces of the treated samples were subjected to the following corrosion tests.

(1) Salt spray test

The test was carried out in accordance with the method of ASTM-B117-73 (JIS-Z-2371), and the results were evaluated according to the following ranking.

5 points No red rust generated
4 points Not more than 10 pin hole red rust generated
3 points Rust spots spread, and slight rust flows observed
2 points Remarkable rust flows observed
1 point Entire surface covered by rust

(2) CASS test

The test was carried out in accordance with the method as stipulated in ASTM-B368-68 (JIS-Z-0201-1971), provided that the pH of the spray solution was 3.5. The evaluation of the results was the same as above.

(3) Outdoor water spray test

A sprinkler was provided on an asphalt-paved area and samples were placed around the sprinkler within 1.4 m in a concentrical arrangement. Water was continuously sprayed at a rate of 0.3 - 0.4 m^3/hr.

(4) Cycle test

The continuous salt spray test stipulated in ASTM-B117-73 (JIS-Z-2371) was conducted for 4 hours, then samples were dried at 60°C for 2 hours and thereafter the samples were placed in an environment of 50°C and 50 % RH for 2 hours. This cycle was repeated.

Example 3

A chromating treatment solution was prepared by dissolving 0.5 part chromic acid anhydride, 0.01 part zinc fluoride and 10 parts t-butanol in 100 parts trichloroethylene to form a homogeneous solution. Samples of the above-described iron-zinc coated bolt

were dipped in the above solution at the refluxing temperature for 1 minute, washed with the solvent vapor and then cooled to room temperature. The samples were subjected to the above-described various tests. The results are indicated in Table 4.

Example 4

A chromating treatment solution was prepared in the same manner as in Example 3 except that 100 parts methylene chloride was used as the solvent. The same samples were treated in the same manner. The same tests were carried out and the results are indicated in Table 4.

Example 5

A chromating treatment solution was prepared in the same manner as in Example 1 except that 100 parts perchlroethylene was used as the solvent. The same samples were treated in the same manner. The same tests were carried out and the results are indicated in Table 4.

Example 6

A chromating treatment solution was prepared by dissolving 15 parts t-butanol and 2 parts chromic acid anhydride in 100 parts trichlorotrifluoroethane to form a homogeneous solution. The same treatment and tests as in Example 3 were repeated and the results as shown in Table 4 were obtained.

Example 7

A chromating treatment solution was prepared by dissolving 15 parts t-butanol, 2 parts chromic acid anhydride and 0.01 part oxalic acid in 100 parts trichlorotrifluoroethane to form a homogeneous solution. The same treatment and tests as in Example 3 were repeated and the results as shown in Table 4 were obtained.

Example 8

In the same manner as in Example 7 except that 0.01 part fumaric acid was used instead of oxalic acid. Immersion for the reaction was carried out at 40°C

(below boiling point) and the results as shown in Table 4 were obtained.

Table 4

Examples		Salt Spray Test (240 hrs)	CASS Test (86 hrs)	Outdoor Water Spray Test (700 hrs)	Cycle Test (90 cycles)
Working Examples	3	5	4	4.5	5
	4	5	5	5	5
	5	5	4	4.5	4.5
	6	5	4	5	5
	7	5	5	5	5
	8	5	5	5	5
Comparative Ex.	1 *	1	1	2	1
	2 *	3	2	4	2

Comparative Ex. 1* Iron-zinc blast plated only, without chromating treatment

2* Iron-zinc blast plated and treated by aqueous chromating

What we claim is:

1. A process for treating the surface of iron materials comprising forming a zinc coating layer on the surface of an iron material by projecting a blast material which is an aggregation of particles each comprising a core comprising substantially iron, intermediate layers of iron-zinc alloys and an outer crust substantially comprising zinc; and treating the thus zinc-coated surface with a non-aqueous chromating composition comprising a chromic acid compound, halogenated hydrocarbon solvent, an alcohol solubilizer.

2. The process as claimed in Claim 1, wherein said zinc crust contains not more than 5 % on the basis of the weight of the crust material of an element selected from a group consisting of copper, aluminum, magnesium, silicon and tin.

3. The process as claimed in Claim 2, wherein said zinc crust contains 3 - 5 % aluminum and 0.2 - 1 % copper.

4. The process as claimed in Claim 1, wherein the weight ratio of the iron core to the zinc crust is 10 - 95 % to 90 - 5 %.

5. The process as claimed in Claim 4, wherein the weight ratio of the iron core to the zinc crust is 10 - 70 % to 90 - 30 %.

6. The process as claimed in Claim 5, wherein the weight ratio of the iron core to the zinc crust is 15 - 65 % to 85 - 35 %.

7. The process as claimed in Claim 1, wherein the halogenated hydrocarbon solvent is a chlorofluorocarbon solvent.

8. The process as claimed in Claim 1, wherein the solubilizer is a secondary or tertiary alcohol in an amount of 1 - 20 parts per 100 parts of the halogenated hydrocarbon solvent.

9. The process as claimed in Claim 8, wherein the solubilizer is tertiary butanol, or tertiary amyl alcohol.

10. The process as claimed in Claim 1, wherein the chromating composition further contains a reaction promotor selected from a group consisting of an organic acid in an amount of 0.001 part to 10 parts per 100 parts of the halogenated hydrocarbon solvent.

11. The process as claimed in Claim 10, wherein the organic acid is a carboxylic acid represented by a general formula $R(COOH)_n$, wherein R is a hydrocarbyl group containing 1 - 19 carbon atoms, and n is an integer of 1 - 3.

12. The process as claimed in Claim 11, wherein the organic acid is selected from a group consisting of formic acid, acetic acid, lactic acid, stearic acid, oxalic acid, fumaric acid, maleic acid, malic acid and a mixture thereof.

13. The process as claimed in Claim 12, wherein the organic acid is contained in an amount of 0.003 - 1 part per 100 parts of the halogenated hydrocarbon solvent.

14. The process as claimed in Claim 13, wherein the organic acid is contained in an amount of 0.005 - 0.5 part per 100 parts of the halogenated hydrocarbon solvent.

15. The process as claimed in Claim 1, wherein the chromating composition further contains hydrogen fluoride as a reaction promotor in an amount of 0.001 to 0.12 part per 100 parts of the halogenated hydrocarbon solvent.

16. The process as claimed in Claim 1, wherein the chromating composition further contains water as a reaction promotor in an amount of 0.001 part per 100 parts of the halogenated hydrocarbon to the solubility limit thereof in the composition.

17. The process as claimed in Claim 1, wherein the chromating composition further contains a stabilizer selected from a groups consisting of amines, quinones, nitro-, azo-, azoxyaromatic compounds, thiourea, dienes,organic nitrite salts, zinc fluoride and zinc

oxide in an amount of 0.001 - 5 parts per 100 parts of halogenated hydrocarbon.

18. The process as claimed in Claim 1, wherein the stabilizer is contained in an amount of 0.05 - 3 parts per 100 parts of the halogenated hydrocarbon solvent.

19. The process as claimed in Claim 18, wherein the stabilizer is contained in an amount of 0.1 - 2 parts per 100 parts of the halogenated hydrocarbon.

20. The process as claimed in Claim 1, wherein the core of blast material is iron, the crust thereof is a zinc alloy containing 3 - 5 % by weight of aluminum and 0.2 - 1 % by weight of copper, the chrcmating composition contains 0.1 - 8 parts of CrO_3, 5 - 20 parts of tertiary butanol or tertiary amyl alcohol and 0.005 - 0.12 parts of a carboxylic acid or hydrogen fluoride per 100 parts of chlorofluorocarbon solvent.

21. The process as claimed in Claim 1, wherein the core of the blast material is iron, the crust thereof is a zinc alloy containing 3 - 5 % by weight of aluminum and 0.2 - 1 % by weight of copper, the chromating composition contains 0.1 - 8 parts of CrO_3, 5 - 20 parts of tertiary butanol or tertiary amyl alcohol and 0,005 - 0,12 part of a carboxylic acid or hydrogen fluoride, 0.05 - 3 parts of a stabilizer per 100 parts of a halogenated hydrocarbon solvent.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number 0177786

EP 85111452.0

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
D,X	JP - A - 56-45 372 (DOUWA TETSUPUN KOGYO K.K.) * Column 5, lines 3-7,20 - column 6, line 1; column 14, lines 8,9,16-18; column 15, lines 9-13; column 18, lines 19,20; column 19, lines 10-20; column 22; column 24, line 3; fig. 1 * & Patent Abstracts of Japan, unexamined applications, M field, vol. 5, no. 101, June 30, 1981 The Patent Office Japanese Government, page 117 M 76 * Kokai-no. 56-45 372 (DOUWA TETSUPUN KOGYO K.K.) *	1-6, 20,21	C 23 C 22/37 C 23 C 24/04 B 24 C 11/00
D,X	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 4, no. 151, October 23, 1980 THE PATENT OFFICE JAPANESE GOVERNMENT page 97 C 28 * Kokai-no. 55-97 476 (NIPPON PAINT K.K.) *	1,7-10 17	TECHNICAL FIELDS SEARCHED (Int. Cl 4) C 23 C B 24 C
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	18-11-1985	SLAMA

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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EUROPEAN SEARCH REPORT

Application number 0177786

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 85111452.0

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
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A	AT - B - 262 712 (DIAMOND ALKALI COMPANY) * Tables; claims * --	1,9-12	
A	CH - A - 449 377 (E.I. DU PONT DE NEMOURS & COMPANY) * Examples 5-19; claims * --	1,8,9, 17	
A	US - A - 4 059 452 (M. NISHIJIMA et al.) * Tables; claims * --	1,10-12	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 23 C B 24 C
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	18-11-1985	SLAMA

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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