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[54] **BLACK OXIDE COATING FOR STAINLESS STEELS**

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[58] **Field of Search** 148/6.11, 6.2, 6.35, 15, 148/27, 28

[56] **References Cited**

UNITED STATES PATENTS

2,537,830	1/1951	Holden	148/15
3,645,802	2/1972	Keough	148/15

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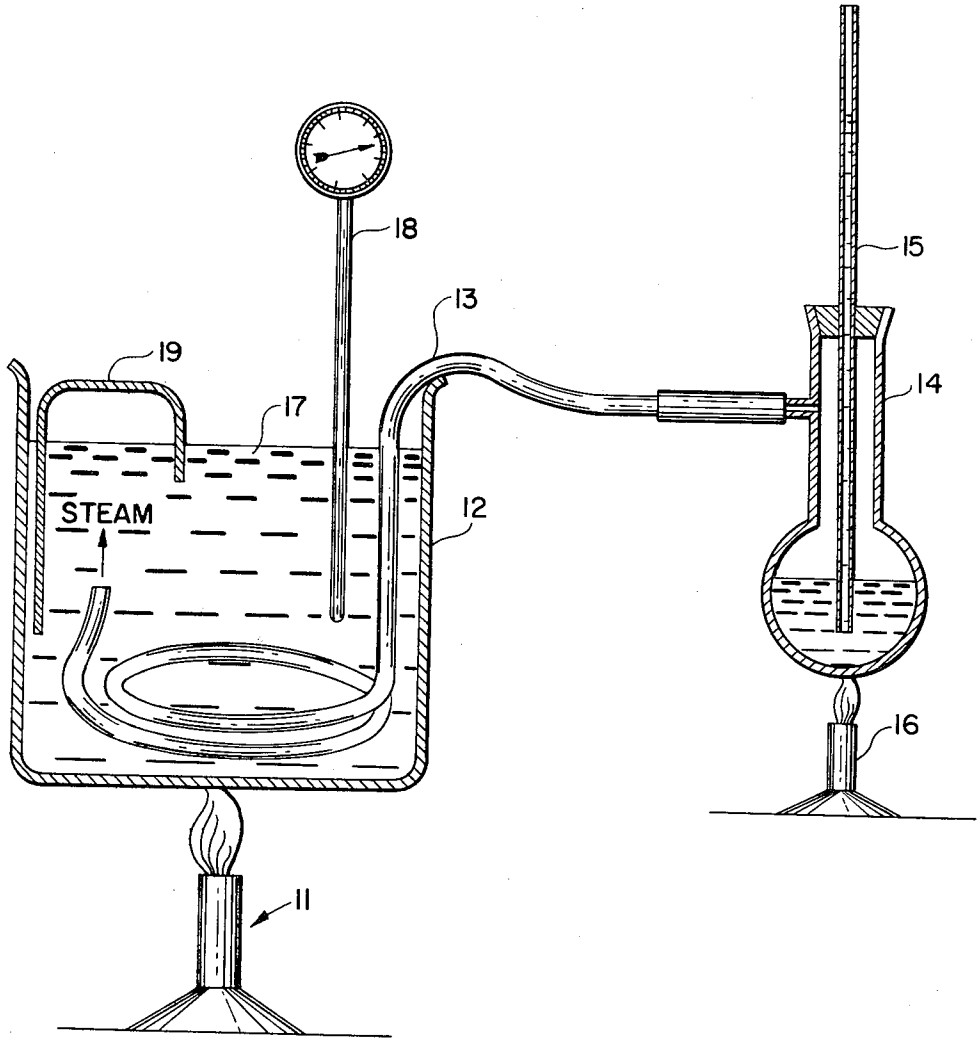
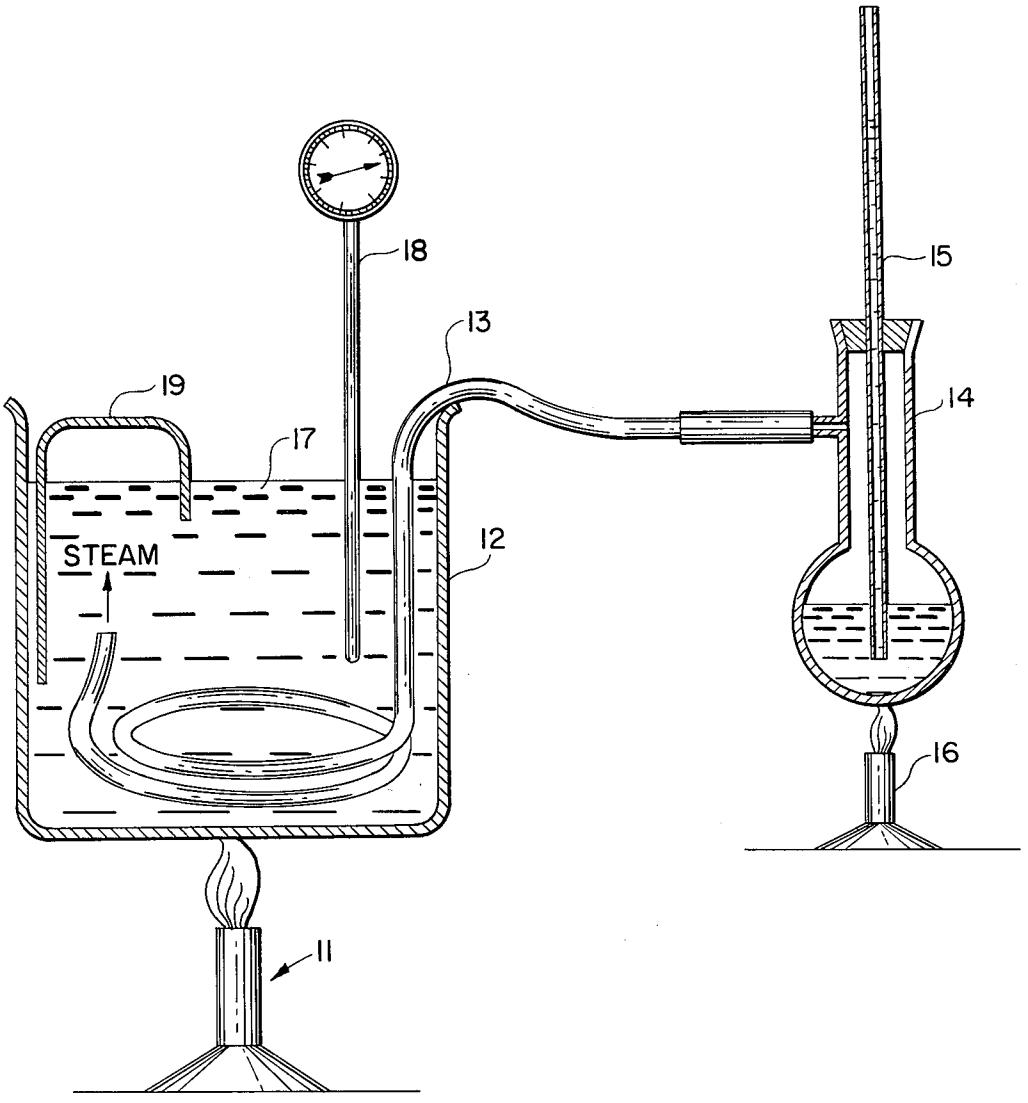
[57] **ABSTRACT**

A method of blackening ferritic and/or martensitic stainless steels which comprises treating said steels by (a) immersing said steel in a fused alkali metal hydroxide-salt bath, which as conventionally produced may initially contain from 3 to 8% water of hydration, for a period of 1–30 minutes, at a temperature of 540°–720°F., and (b) continually adding water during the heat treatment in step (a); said water can be introduced in the form of steam to replenish the original water of hydration of the fused bath and the amount of water added ranges from an effective amount to about 15% by weight of the fused salt mixture. This addition of water in the ranges 1–15% and 3–8% replenishes and reinvigorates the molten salt bath so that the bath likewise has a satisfactory water content based on the molten salt mixture. A preferred fused salt mixture is the eutectic mixture of sodium and potassium hydroxide, and an additive agent such as an alkali metal molybdate may be added to the fused salt mix.

12 Claims, 1 Drawing Figure

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BLACK OXIDE COATING FOR STAINLESS STEELS

The present invention relates to a process for producing a black-colored oxide coating on the surface of ferritic or martensitic-type stainless steel alloys by means of heating said steel in contact with an initial fused potassium hydroxide, sodium hydroxide, or mixture of alkali metal hydroxides whereinto steam is injected for the purpose of maintaining in the fused bath a concentration of water which may range from a small but effective percentage up to approximately 15% by weight of the fused salt mixture. The steam is continually added during the entire heating step of the process which is conducted under open conditions at a temperature of 540°–720° F. for 1–30 minutes to replenish and restore the original content and consequent fused bath activity. It should be understood, however, that in this invention the introduction of steam is not used in limiting sense but as an efficient and convenient way to supplement the loss of water from the fused salt bath due to evaporation.

PRIOR ART

The prior art pertinent to the present invention consists of use of molten alkaline or neutral salt baths, which in all cases are substantially anhydrous and contain at least one oxidizing agent.

Thus, in Pat. No. 2,479,979, Spence et al., (Hooker) teach a procedure using an anhydrous fused alkali bath with 5–10% of an oxidizing agent at temperatures of 550°–1100° F. for 1–25 minutes. Pat. Nos. 2,618,578 by Kreml (Armco), 2,537,035 by Clingan (Armco), and 2,542,994 by Cobb (Armco) describe the use of various molten alkali metal dichromate compositions, all of which appear to be anhydrous, in blackening stainless steel alloys. In Pat. No. 2,431,986 by Clingan (Armco), an anhydrous molten salt bath consisting of alkali metal nitrates is claimed to produce in 5–40 minutes colored coating on stainless steel surfaces at 730°–840° F.

The method of the present invention is conducted in the fussed bath at high temperature, but contrasted with the art above, water (steam) is continually introduced in order to maintain a small but effective water content in the fused salt bath.

There is a current commercial demand for a strongly adherent black coating on steels with high mechanical and structural strength, namely, on stainless steels. Such steel is known to be more resistant to chemical attack. The present process is designed to satisfy a need and is made for blackening martensitic and/or ferritic stainless steel of the AISI 400 series.

The present process is tailored specially for the alloys embodying chiefly iron and chromium which are less expensive than those austenitic type embodying iron, chromium and nickel. The success of the present with the so-called ferritic and martensitic stainless steel varities makes is commerically important in industry for utilization in the manufacture of automotive trim, windshield wipers, etc., where corrosion resistance is a prime concern and yet, other properties related to ease of manufacture and strength in use are also important.

FIG. 1 shows a schematic illustration of a preferred form of utilizing the present invention, **11** — Meker burner, **12** — open container, **13** — steam coils, **14** — stem generator, **15** — pressure equalizing tube, **16** — Meker burner or electric hotplate, **17** — fused salt mixture, **18** — thermometer, **19** — shield to prevent splashing and to facilitate retainment of steam in the molten bath.

GENERALIZED DESCRIPTION OF THE PROCESS

As a substrate material, a stainless steel of the iron-chromium type is utilized. Such steels are described in *The Making, Shaping and Treating of Steel* (U.S. Steel Corporation), 8, 1964, Chapter 45, especially page 1112, and also *The Encyclopedia of Chemical Technology*, II, (Interscience-Wiley) Volume 18, 1969, at pages 790–791. In general, in utilizing AISI-type members, those designated in the 400 series on page 791 (ECT above) are operable for the present invention.

With reference to the alkali metal hydroxide, an eutectic mixture of sodium and potassium hydroxides is preferred for the present invention due to the advantageously lower melting point, although under special circumstances, sodium hydroxide or potassium hydroxide may also be used in order of preference. sodium and potassium hydroxide are utilized as commercially received solids in form of flake or lumps. Commercial anhydrous sodium hydroxide is available with less than 0.5% of moisture and also at 3% moisture, and potassium hydroxide moisture content ranges from 6 to 8%. Definitive test material is noted in *The Encyclopedia of Chemical Technology*, II, (Interscience-Wiley) 1968, Volume 1, page 753, and Volume 16, page 391, respectively.

The thrust of this invention is in preferably continually adding water during the treating process to replenish and restore or maintain and augment the water content initially present in the fused salt mixture. The utilization of steam is a convenient way to supply water under the employed conditions, but this invention is by no means limited to this method of water addition. Intermittent steam or water addition may be utilized, but is not as efficient.

Heating is accomplished in an open vessel by dipping or suspending the metal article beneath the surface of a fused bath. By definition, "fused salt bath" in the present specification means sodium or potassium hydroxide or mixture of the same, which contain 3–8% water of hydration and as normally sold. Further, removal of water from commercial potassium hydroxide down to less than 6–8% would require extraordinary methods such as vacuum or by heating the fused material at temperatures higher than 550° F. for prolonged periods of time.

When the metal article is immersed in the fused salt bath and is heated for 2–30 minutes at a temperature of 540°–720° F., water in the form of steam, preferably dry steam, is added through steam jets immersed in the molten bath and in an amount so that the total retained water amounts to about 2–15% by weight of the initial fused salt mixture. More restrictive but more effective ranges for water addition are progressively about 2–12% and 3–8% by weight as above. At the end of treatment the stainless steel article, such as an automobile window wiper frame, is coated with a thin and very tight oxide layer, and is removed in blackened condition.

A preferred modus utilizes an eutectic mixture of fused salt (about 50% NaOH - 50% KOH) as a starting material, and into the mix may be added an oxidizing agent in the extent of 5–10% by weight of the initial salt mixture; as additive preferably an alkali metal molyb-

date is employed. Where the term "alkali metal" is used herein, it refers to sodium and potassium, e.g., hydroxides and molybdates. The utilization of an eutectic mix of sodium and potassium hydroxide, while not essential, is preferred because of a lower melting point which, in turn, enables one to discontinue the heat overnight without solidifying the bath. In other words, one may cool the bath down to 300°F. and still have a liquid. As oxidizing additives, an alkali metal molybdate such as sodium molybdate is preferred and utilized in amounts usually of 5–10% by weight of the fused salt mix. Also operable are equivalent chromates and permanganates.

WATER CONTENT

When the commercial grades of granular sodium and potassium hydroxide are intimately mixed in equal weight proportions, calculations confirmable by chemical analysis show that the mixture will contain approximately 3—5% water by weight. We have discovered that when such a mixture is heated in an open vessel until melted and heating is continued until a temperature in the range of approximately 540°–720° F. is attained, the resulting fused salt bath is effective in imparting black coatings to AISI 400 series stainless steels immersed therein. The bath is found to be effective, however, only so long as a substantial portion of water is retained, and the effectiveness is virtually lost if the bath is allowed to become substantially anhydrous due to evaporation.

This discovery is illustrated by an experiment in which 1000 grams each of commerical granular sodium and potassium hydroxides were intimately admixed. The mixture was found to contain 4.7% by weight of water. The mixture was placed in an open beaker made of AISI series 300 stainless steel and rapidly heated with a Meker burner. Approximately one-half hour was required to melt the mixture and raise the temperature to 580° F. Thereafter the temperature was maintained at 580° ± 10° F. for several hours while periodic tests were performed to evaluate the effectiveness of the molten mixture in blackening AISI 434 stainless steel. Samples of the molten mixture were taken periodically during this period and analyzed quantitatively for carbonate ion and hydroxide ion by the alkalimetric titration method described in F. J. Welcher, Ed., "Standard Methods for Chemical Analysis", Van Nostrand Reinhold Co. (1963), Vol. IIA, page 602. The sum of the sodium and potassium percentages present in each titration sample was calculated from (1) the total alkalinity value of the sample, and (2) the ratio of sodium and potassium in the original mixture. The percentage of water in each sample was determined by difference, i.e., by deducting from 100% the sum of the carbonate ion, sodium ion, sodium and potassium percentages.

During the aforesaid testing procedure, the water content of the molten mixture was also assayed by a second method wherein the entire bath vessel and contents were weighed periodically. By making corrections for (1) sampling losses, (2) drag-out losses, and (3) carbonate accumulation resulting from reaction between air-borne carbon dioxide and the alkaline metal hydroxides, a net bath weight was obtained. Differences between the original net bath weight of 2000 grams and subsequent experimentally determined values for the net bath weight were attributed to changes in the water content from the original 4.7% by weight.

As shown in Tests Nos. 1 and 2 in Table I, the molten mixture was initially effecitve in imparting a desirable black color to the stainless steel. As the bath aged, however, its water content progressively descreased due to evaporation until ultimately the blackening power was lost (Tests Nos. 4, 5 and 6).

TABLE I

Treatment of AISI 434 Stainless Steel Specimens With Molten Mixture of 50% (Wt.) Granular Sodium Hydroxide - 50% (Wt.) Granular Potassium Hydroxide [a]

Test No.	Bath Age, Minutes at 580°F. [b]	Specimen Immersion Time, Minutes	Average Water Content Wt.% [c]	Appearance of Coating on Test Specimens	
				Apparent Thickness	Color
1	3	12	4.4	Thick	Black with smut
2	40	12	3.4	Moderate	Black
3	82	12	2.5	Thin	Blue-Black
4	140	12	1.8	Thin	Brown
5	211	12	1.3	Thin	Brown
6	309	60	0.9	Thin	Brown

[a] Initial net weight of molten mixture was 2000 grams. Treatment temperature was 580 ± 10° F.
[b] Elapsed time between instant when bath first reached 580° F. and instant when test specimen was immersed.
[c] Average of values determined by two methods described in text.

We have discovered that the loss of effectiveness discussed and illustrated in the preceding paragraphs can be prevented or reversed by injecting water, most conveniently in the form of steam, directly into the molten bath. This is illustrated by a continuation of the experiment described in the preceding paragraph and in Table I wherein steam was injected into the deactivated bath until the water content exceeded 8% by weight. The stem was injected into the molten mixture over a period of 110 minutes by means of an apparatus essentially identical to that in FIG. 1. Upon termination of the steam injection, the molten mixture was maintained at 580° ± 10° F. for several hours while periodic tests were performed to assay the water content and to evaluate the effectiveness in blackening AISI 434 stainless steel. The results are presented in Table II.

A comparison of these results with those in Table I indicates that the steaming process restored the effectiveness of the bath for blackening and that the effectiveness was then retained until in Test No. 10 the water content was again allowed to reach a low value due to evaporation.

TABLE II

Treatment of AISI 434 Stainless Steel Specimens With Steam-Reactivated Molten Mixture of 50% (Wt.) Granular Sodium Hydroxide - 50% (Wt.) Granular Potassium Hydroxide [a]

Test No.	Bath Age, Minutes at 580° F. [b]	Specimen Immersion Time, Minutes	Average Water Content, WT.% [c]	Appearance of Coating on Test Specimen	
				Apparent Thickness	Color
7	3	12	8.4	Thick	Black with smut
8	27	12	6.1	Moderate	Black with smut
9	65	12	3.6	Moderate	Black with smut
10	169	12	less than 2.0	Thin	Light Blue-Brown

[a] Reactivated bath described in Table I was steamed in the molten state until water content exceeded 8%.

[b] Elapsed time between termination of steaming step and immersion of test specimen.

[c] Average of values determined by two methods cited in text.

Based on these experiments and data from the literature, the water content required for effective blackening its approximately 2.3%, but it may range up from 1% in some special circumstances. The important point is that injection of steam produces beneficial results, and that those skilled in the art will be capable of adjusting the steam injection rate so as to maintain the desired degree of effectiveness as to water content.

In connection with this, it was found that when steam is injected into the bath at a relatively low rate and a relatively low but efficient water concentration is thereby maintained, the resulting coatings tend to possess a relatively thin and shiny appearance. Conversely, when the steam injection rate is relatively high and the water concentration is relatively high but within the range covered by our claims, the resultant coatings tend to possess a relatively thick and dull appearance. This invention thus affords the user a broad selection of attainable results.

The following examples are illustrative of the practice of this invention; however, the invention is not intended to be limited by the details set forth in these examples.

EXAMPLE I

Effect of Water Addition on the Blackening Process

The following mixture consisting of:

KOH, Flake	475 g.
NaOH, Flake	475 g.
Na_2MoO_4	50 g.
	1000 g.

was heated and melted in an AISI 300 series stainless steel beaker. The vessel was weighed from time to time in order to observe eventual loss of weight. After melting, the above mixture was heated and maintained at a temperature of 550°–600 F., while specimens of AISI 434 stainless steel were blackened by immersing them for 5–10 minutes into the molten mixture. The coatings were black, thin, and very tight; they could not be rubbed off even by rubbing hard with steel wool. After 2 ½hours, the net weight dropped to 958 grams (corrected for dragout losses). The loss of 4.2% was attributed to the evaporation of water initially present in the mixture. the observed weight loss paralleled the loss of blackening activity; specimens immersed for 10 minutes acquired only very thin, irridescent coatings. The bath was allowed to cool down, then 41 grams of water were added. The heating was resumed and the bath showed that its blackening activity toward AISI 434 stainless steel was restored.

EXAMPLE II

Molten Bath Activity Depending on Introduction of Steam

In order to prevent or reverse the loss of small amounts of water necessary for the blackening process, a continual water addition was an essential factor. An apparatus described in FIG. 1 was set up. The initial bath composition was identical with one described in Example I. Bath activity in blackening of AISI 434 stainless steel was studied as a function of water absorption via steaming, using weight changes to assay water content changes. The bath at 575° F. was active at the initial net weight as previously described in Example I, as well as when the net weight gain was about 4%. When the net bath weight loss reached about 3%, the activity was diminished.

Addition of 100 grams of Na_2CO_3 did not destroy the activity of the bath. Therefore, pick-up of CO_2 from the air should not be considered detrimental to the bath and no special precautions to exclude the contact with the same were undertaken.

EXAMPLE III

Molybdate-Free Molten KOH-NaOH Bath With Steam Introduction

The following initial bath composition was employed in this experiment:

KOH, Flake	1000 g.
NaOH, Flake	1000 g.
	2000 g.

Water content was varied by changing the rate of steaming so that the net bath weight was changing from 1927 to 2160 g. Satisfactory coatings on AISI 430 stainless steel panels were obtained at the net weights above 1960 g. At the net weight of 2160 g. and 480° F. 430 stainless steel panels were still reacting but hydrogen evolution did not stop even after 20 minutes of treatment and the resulting coatings was very smutty and of poor adherence. At 600° F. and at net bath weight of 2010 to 2065 g., the coating process was very fast and in 2 minute contact time a satisfactory coating was formed.

EXAMPLE IV

Effect of Major Process Variables on Appearance and Corrosion Resistance of AISI 430 Stainless Steel

As set out in Table III and in a number of experiments therein, stainless steel panels were black coated by the process of the present invention and then challenged by the CASS test (ASTM B368-68), which is a corrosion test utilizing a mixture of a copper chloride and acetic acid in order to accelerate a salt spray. The resistance to corrosion is measured under a sliding scale of 1 to 10. The results uniformly showed that there was good to excellent resistance to corrosion in the panels noted. Additionally, in Run No. 3, the panel was prior etched by a composition which was a mixture of hydrofluoric and nitric acid.

The results also showed that a satisfactory adherent, black coating may be obtained by the present process, which, dependent upon water content and temperature, may be varied from dull to shiny, dependent upon the market request.

TABLE III

Treatment of AISI 430 Stainless Steel Under Various Conditions

Bath consisting of initial 2000 g. of NaOH + KOH eutectic mixture (1:1 ratio by weight) with 0–10% of Na_2MoO_4. In each experiment 5 panels (2" × 1⅓") of AISI 430 stainless steel were simultaneously processed under different sets of conditions. The water content was maintained constant throughout an experiment by the addition of steam.

	Experiment Number										
	1	2	3[a]	4	5	6	7	8	9	10	11
% of Sodium Molybdate	0	0	0	5	5	5	5	5	5	10	10
Bath Temperature, ° F.	580	580	580–595	580	580	580	550	620	580	580	580
Contact Time, Minutes	10	10	10	10	10	30	10	10	10	10	10
Net Bath Weight[b]	2045	2020	2020	2049	2020	2021	2017	2020	1989	2052	2024
Estimated Water Content, gr.[c]	145	120	120	149	120	121	117	120	89	152	124
% of Water in Bath	7.1	5.9	5.9	7.2	5.9	6.0	5.8	5.9	4.5	7.4	6.1
Gas Evolution Rate	Fast	Fast	Fast	Fast	Fast	Fast	Slow	Very fast	Med.	Fast	Fast
Gas Cease Time, Minutes	3–4	4	4	5–6	7	7–8	7–10	2–3	8	7–8	9–10
Coating (Reflectiveness*	D	S	D	D	S	S	D	S	S	D	D
Appearance (Color - Smut*	B Sm	Bl-B	B Sm	Bl-B	Bl Sm	Bl-B	Bl-B	Bl-B	Bl-B	B Sm	B Sm
Average Corrosion resistance[d]	6.0	6.9	5.8	8.7	4.5	6.6	2.5	8.2	8.8	5.1	8.5

[a]Panels etched in a mixed hydrofluoric/nitric acid etching composition, rinsed and dried prior to blackening.
[b]Corrected for drag-out (panels weighed with solidified drag-out, then washed, dried and weighed again). Drag-out represents a small amount of bath material.
[c]Commercial caustic soda (NaOH) and caustic potash (KOH) flake contain about 6% of water (Encyclopedia of Chemical Technology, II, Volume 1, page 753, and Volume 16, page 391). Therefore, an initial charge of 2000 g. is assumed to contain 120 g. of water ± amount of water introduced or evaporated in the form of steam.
[d]Cass Test ASTM B368-68. All the panels submitted to maximum of 4 cycles consisting of 16 hours of active exposure in the Cass cabinet. Observations were made after each cycle and panels with signs of corrosion were removed. Number of cycles before failure and the extent of corrosion were rated as follows:
10 points = no corrosion after 4 cycles
7–9 points = no corrosion after 3 cycles
3–6 points = no corrosion after 2 cycles
1–2 points = corrosion during first cycle
* = Dull
S = Shiny
Bl = Blue
B = Black
Sm = Smut

What is claimed is:

1. A method of blackening ferritic and martensitic stainless steels which comprises immersing said steels for a period of 1–30 minutes in a fused alkali metal hydroxide salt bath, wherein the alkali metal is selected from the group consisting of sodium and potassium, which bath contains an effective amount of water maintained by subsequent addition to the bath at about 1–15% by weight of said bath, and wherein said bath is maintained at a temperature of about 510°–720° F.

2. The method of claim **1,** wherein water is continuously added to the fused salt bath in order to maintain a concentration of 1–15% by weight of water in said bath.

3. The method of claim **1,** wherein water is intermittently added to the fused salt bath in order to maintain a concentration of 1–15% by weight of water in said bath.

4. The process of claim **2,** wherein water is introduced into the fused salt bath in the form of steam.

5. The process of claim **2,** wherein water is introduced into the fused salt in the form of dry steam.

6. The method of claim **1,** wherein the water content is maintained at about 2–12% by weight of the fused salt mixture.

7. The method of claim **1,** wherein the water content is maintained at about 3–8% by weight of the fused salt mixture.

8. The method of claim **1,** wherein alkali metal hydroxide is selected from at least one member of the group consisting of sodium hydroxide and potassium hydroxide.

9. The method of claim **1,** wherein the fused salt bath is an eutectic mixture of sodium and potassium hydroxides.

10. The method of claim **1,** wherein the stainless steel is selected from at least one member of the group consisting of the AISI 400 series stainless steels.

11. The method of claim **1,** wherein the temperature is maintained at 540°–650° F.

12. The method of claim **1,** wherein an oxidizing agent is added in the amount of 5–10% by weight of the fused salt mixture, and said oxidizing agent is selected from at least one member of the group consisting of alkali metal molybdates. chromates and permanganates.

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