April 26, 1955 J. X. FOUCRY ET AL 2,707,159

WEAR-RESISTANT FERROUS METAL ARTICLES AND THEIR PRODUCTION

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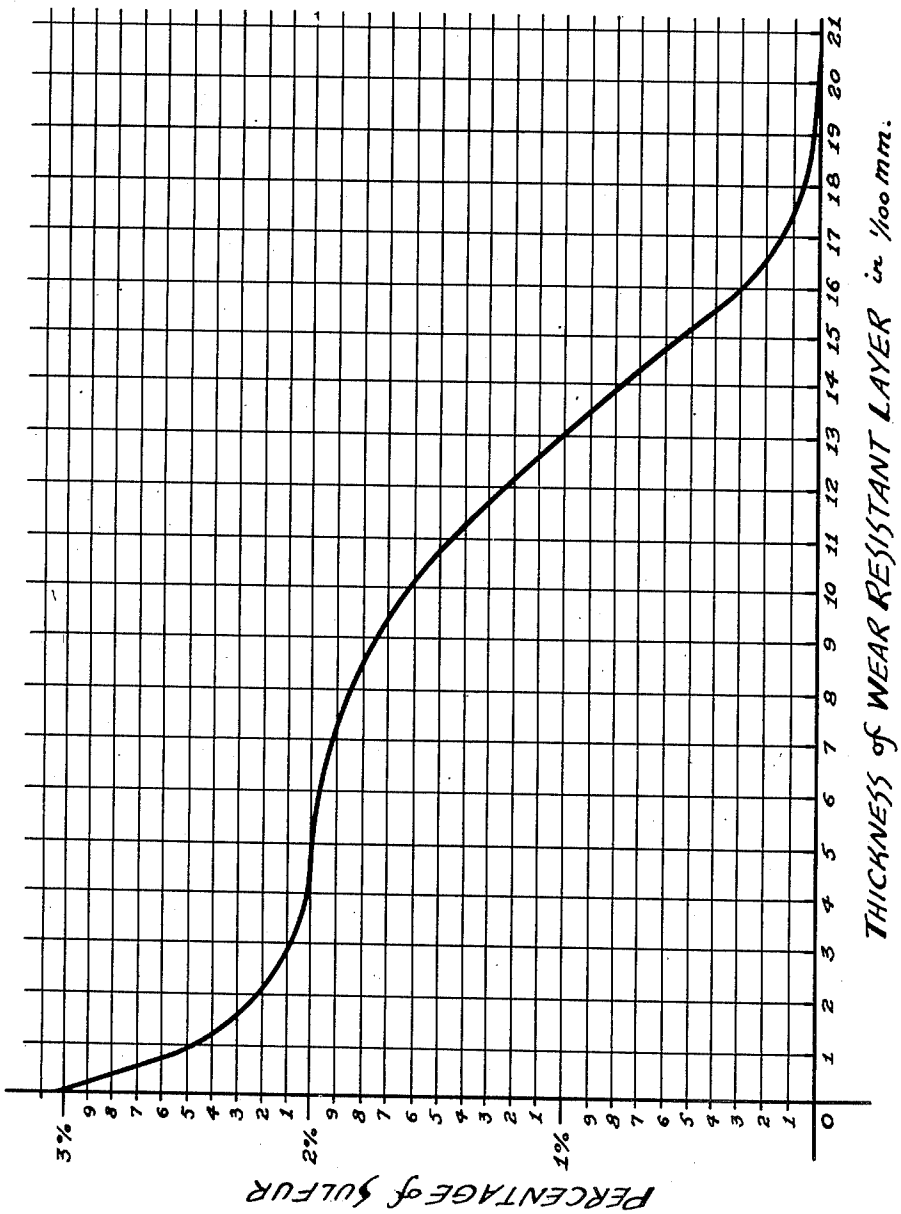


FIG. 1.

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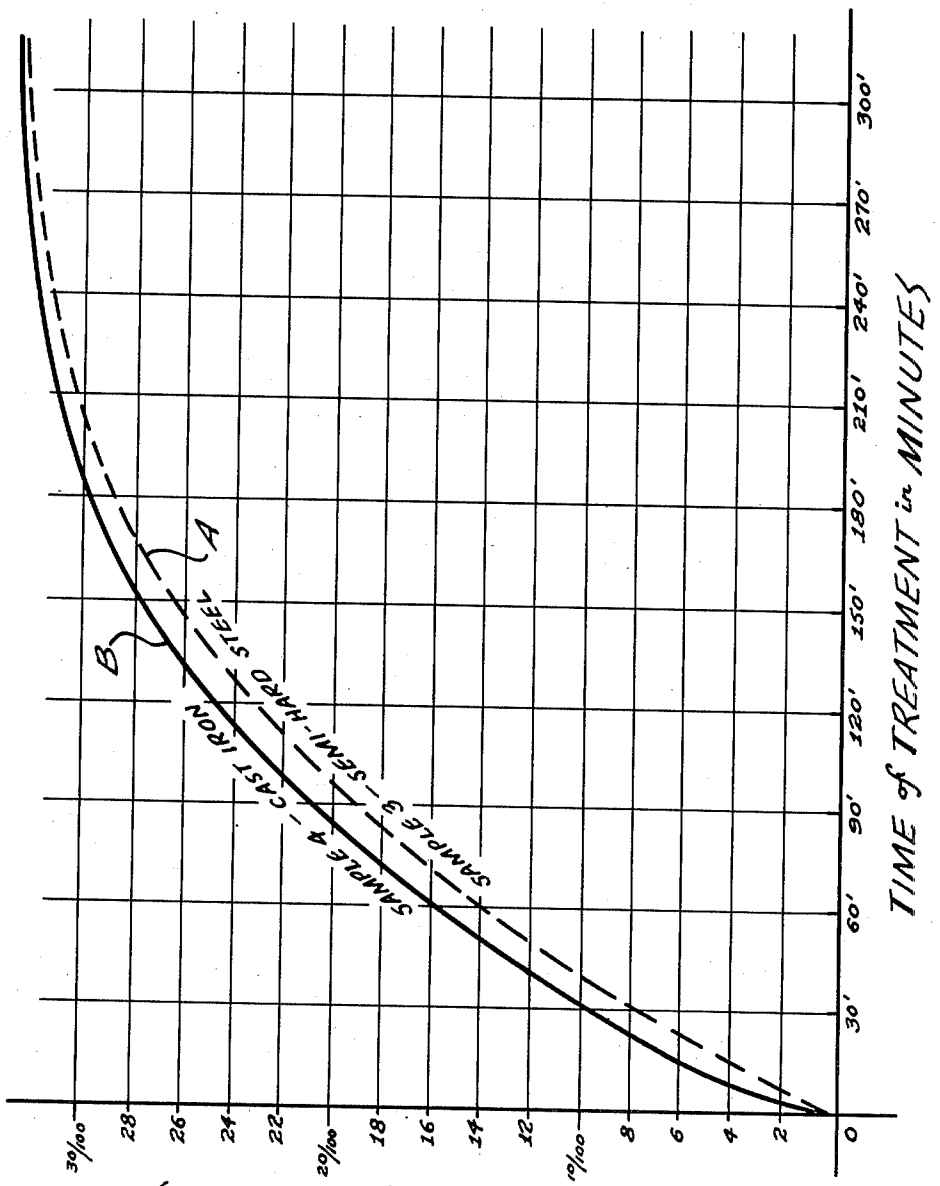


FIG. 2.

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2,707,159

WEAR-RESISTANT FERROUS METAL ARTICLES AND THEIR PRODUCTION

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Application January 13, 1951, Serial No. 205,946

Claims priority, application France February 19, 1947

26 Claims. (Cl. 148—6.11)

The present invention relates to a method of producing on ferrous metal pieces, such as machine elements or other parts made of iron, iron alloys or steel, surface layers having an extraordinarily high resistance to wear and a reduced coefficient of friction. The invention relates also to highly wear-resistant ferrous metal articles and to metal treatment compositions effective for producing them.

Ferrous metal articles having a low coefficient of friction and a high resistance to wear are needed for a great many uses, especially in the automotive industries.

According to this invention, it has been found that articles serving that need can be obtained by incorporating sulfur in a chemically combined form in superficial layers of ferrous metal pieces, to a considerable depth from the surfaces into the base metal of the pieces. The presence of substantial quantities of sulfur in ferrous metals generally is scrupulously avoided, sulfur being considered a serious contaminant of the base metal. The ferrous metal articles here provided, however, have superficial layers substantially enriched in combined sulfur to a depth well over 0.05 mm. and up to a depth of several tenths of a millimeter, depending upon the intensity or duration of the treatment applied. The sulfurized layers so formed possess a surprisingly increased resistance to wear and a considerably reduced coefficient of friction, while the base metals bearing these layers suffer no deterioration of their desirable properties.

Articles having these important characteristics can be produced by subjecting ferrous metal pieces at elevated temperatures to the action of sulfur in the form of a sulfur compound or salt in which the sulfur is incompletely oxidized, i. e., is present in a chemically combined form other than that of sulfate sulfur. Sulfur in this form is referred to herein as active sulfur.

An effective procedure is to expose surfaces of the ferrous metal pieces at an elevated temperature to the action of such a sulfur compound in a molten state. The compound applied may be an oxygen-free sulfur salt, such as a molten alkali sulfide or sulfocyanate.

The molten active sulfur compound is applied advantageously as part of a molten salt bath in which the metal pieces are treated by simple immersion for a suitable period, depending upon the desired depth of the treatment, and which also contains alkali metal or alkaline earth metal salts serving as stabilizers or both as carriers or diluents and stabilizers. The active sulfur content of the bath needs be only about 0.4 to 2 per cent of its weight. The bath as a whole is composed of salts that melt at a temperature well below the elevated treatment temperature, and the constituents are selected to maintain reducing conditions in the bath, which preserve the activity of the sulfur content. For this purpose, a substantial content of an alkaline cyanide and an alkaline cyanate is particularly effective. An alkaline cyanide alone may be used as a reducing or stabilizing agent, but this becomes converted partially into alkaline cyanate when melted into the bath.

Various salts containing sulfur in an incompletely oxidized state may be used as the source of active sulfur for such molten bath compositions. Useful compounds are the alkaline sulfides, sulfites, thiosulfates, sulfocyanates and thiourea salts for example: sodium, potassium and lithium sulfides, sulfites, thiosulfates, sulfocyanates and thiourea salts of said metals, which may be used individually or as mixtures of two or more of such compounds. When a sulfite or thiosulfate, e. g. sodium sulfite and/or sodium thiosulfate, is employed in the presence of an alkaline cyanide, e. g. sodium cyanide, the active sulfur in the molten bath is present as sulfide sulfur, by reason of the reactions:

(a) $Na_2SO_3 + 3NaCN \rightarrow 3NaCNO + Na_2S$

(b) $Na_2S_2O_3 + 4NaCN \rightarrow 3NaCNO + Na_2S + NaSCN$

The use of a sulfocyanate with an alkaline cyanide also yields sufide sulfur in the molten bath, as well as sulfocyanate.

A considerable part, even a major proportion, of the salt bath composition may consist of compounds that serve only as carriers or diluents, for example, alkali or alkaline earth carbonates or chlorides, or other alkali metal or alkaline earth metal salts having suitable melting points and no objectionable oxidizing or metallurgical properties. Only a minor proportion of the bath composition need be composed of the reducing or stabilizing compounds and the active sulfur compound or compounds. Very efficient operation can be assured by maintaining in the molten bath, in addition to the active sulfur compound or compounds, about 25 per cent or more by weight of cyanide and cyanate with these and other constituents proportioned to give the composition the desired fusion temperature.

The salt composition preferably is one that melts at a temperature below 500° C. The desired sulfurizing action then is obtained by immersing ferrous metal pieces in the molten composition at limited temperatures above 500° C., temperatures of the order of 550° C. to 600° C. being particularly effective. The period of immersion varies with the depth of the desired sulfurized layer, but should be at least 20 minutes. For example, a layer at least 0.1 mm. deep can be obtained on cast iron pieces by immersing them for about 30 minutes in a bath at about 580° C., while immersion of similar pieces in the same bath for about three hours will produce a sulfurized layer about 0.3 mm. deep.

A surprising feature of the practice of this invention is that it greatly enhances the wear resistance of the treated surface layers but brings about little or no increase in their hardness. No appreciable carburizing or nitriding action occurs, even though cyanides and cyanates are present in the treatment bath, and it is not necessary to use treatment temperatures high enough to cause objectionable side effects or phase changes in the base metal.

The following four examples constitute illustrative embodiments of the invention showing our treatment baths or compositions, before and after being molten, used in producing the surface layers on the ferrous metal pieces which impart extraordinary wear resistance and reduced coefficient of friction. The parts are expressed as percentage by weight.

EXAMPLE I

	Per cent
NaCN	34
Na_2SO_3	7
KCl and NaCl	27
Na_2CO_3	16
K_2CO_3	16

Upon melting at 480° C., the bath had the following analysis and is designated as bath "S_1."

	Per cent
NaCNS	1.6
Na_2S	1.8
Na_2CO_3	18.9
K_2CO_3	18.9
NaCl+KCl	26.8
NaCN	25
NaCNO	7.2

The active sulfur content of this bath equals 1.35%.

EXAMPLE II

	Per cent
NaSCN	4
NaCN	32
Chlorides and carbonates	64

After melting at 480° C. the bath had the following analysis and is designated as bath "S_2."

	Per cent
S in Na_2S	0.9
S in NaCNS	0.8
NaCN	25
NaCNO	1.2

Chlorides and carbonates to 100%.

EXAMPLE III

	Per cent
NaCN	95
Na_2SO_3	5

After melting at 480° C. the bath showed the following composition and is designated as bath "S_3."

	Per cent
NaCN	85.9
NaCNO	6.5
Na_2S	1.5
NaSCN	1.6
Na_2CO_3	4.5

The active sulfur content of this bath is 1.27%.

EXAMPLE IV

Bath S_4:	Per cent
S in Na_2S } S in NaCNS }	1.58
NaCN	4
NaCNO	5

Chlorides and carbonates to 100%.

This bath, containing a very low percentage of cyanide and cyanate, was used to show that the high concentrations of such products used in nitriding or carbonizing baths are not necessary in the baths of this invention.

Bath N:	
NaCN	58%.
NaCNO	12%.
NaCl etc	bal. to 100%.
S	None.

This bath is a commercial nitriding bath and was used for comparative purposes.

Test or sample pieces of the following ferrous metals were used for evaluating this invention. Such test or sample piece or pieces made from ferrous metals of the stated compositions are generally designated herein by the sample number.

Sample No. 1.—Extra-mild steel

C=0.06
Mn=0.20
Cr=0
Ni=0
S and P<0.05

Sample No. 2.—Semi-mild steel

C=0.18/0.20
Mn=0.72
Cr=0
Ni=0
Mo=0
S and P<0.05

Sample No. 3.—Semi-hard Manganese steel

C=0.40
Mn=0.90/1
Cr=0
Ni=0
S and P<0.05

Sample No. 4.—Cylinder cast iron

C total=3.25/3.20
C combined=0.50
Si=2
Mn=0.70
P=0.20
S=0.10
Cr=0.35/0.40
Ni=0.15/0.20
Mo=0.40/0.45

(The sample was taken from a "Hercules" diesel engine.)

The test pieces were formed as ground cylinders of 6.35 mm. diameter. Test pieces of three of the four illustrative ferrous metals were dipped into each of the five illustrative baths and held therein at a temperature of 580° C. for a period of 30 minutes. A duplicate sample was set aside as a standard or control for comparative purposes.

After treatment, the samples of the various ferrous metals were subjected to torsion and wear tests in the conventional Faville-Levally machine which is normally used for the test of lubricants and comprises two V-shaped jaws with the sides of the V's diverging to form a right angle. These jaws are made of hardened semi-hard steel and are arranged to permit symmetrical clamping under a predetermined adjustable pressure on a cylindrical test piece connected to a rotary driving member by means of a pin of 2 mms. diameter extending diametrically through an end of the test piece. In the torsion tests, the fastening pin of the test piece was a copper wire and in the wear tests a steel wire.

The pressure on the jaws and the corresponding driving torque which is necessary for rotating the test piece relative to the jaws are indicated through conventional measuring devices. It is obvious that for a given pressure on the jaws the driving torque is proportional to the coefficient of surface friction of the test pieces.

In all the tests, the jaws were lubricated by means of paraffin oil except for the wear tests made on the test pieces of Sample 3 for which no lubricant was used.

The following tables give for each sample both the values of the torques in pounds per inch for different pressures in pounds and the value of the pressure applied on the jaws of the testing machine at the moment of the jamming of the various test pieces as indicated by the breaking of the test pieces.

TABLE I
(Sample 1)

Pressures, lbs.	500	1,000	1,500	2,000	2,750	Jamming pressure, lbs.
	Torques (lbs. per inch)					
Treated in:						
"S_1"	4	13	20	29	36	2,900
"S_2"	4	12	24	29	36	2,900
"S_3"	3	12	23	28	34	3,000
"S_4"	4	12	24	29	36	2,900
"N"	3	13	30			1,600
Control	3					750

TABLE II
(Sample 2)

Pressures, lbs.	500	1,000	1,500	2,000	2,500	Jamming pressure, lbs.
	Torques (lbs. per inch)					
Treated in:						
"S_1"	5	15	23	26	32	2,750
"S_2"	5	15	23	28	32	2,750
"S_3"	5	15	24	28	34	2,700
"S_4"	5	15	24	30	35	2,650
"N"	6	16				1,250
Control	4					900

TABLE III
(Sample 4)

Pressures, lbs.	500	750	1,000	1,250	Jamming pressure, lbs.
	Torques (lbs. per inch)				
Treated in:					
"S_1"					
"S_2"	3	7	9	13	non-jammed at 2,900.
"S_3"					
"S_4"	4	7	9	13	
"N"	4	6	8	12	1,250.
Control	3	5	8	14 to 32	1,250 in 30 sec.

It appears from the above results of the tests that at the beginning of each test the coefficient of friction of the treated test pieces is practically the same or even sometimes slightly higher than that of the untreated pieces. This characteristic is believed to be due to the formation at the surface of the test pieces of a very thin dull surface layer during the treatment in the bath, which disappears almost immediately upon subjecting the pieces to frictional engagement. Upon increasing the loads, the coefficient of friction becomes clearly lower for the test pieces treated according to this invention than for the untreated or nitrided test pieces. The reduction in the coefficient of friction is shown by the increased load required to cause jamming.

The wear test results described hereinafter in Tables

IV to VII are still clearer indications of the increased wear resistance of pieces treated according to this invention. The tests, the results of which are given in the following tables were performed on the same Faville-Levally machine as the above quoted tests. In each evaluation, ferrous metal test pieces of Samples 1, 2 and 4 as previously described, were rotated in the machine under a load of 1250 lbs. on the jaws which were lubricated with paraffin oil. Tests on Sample 3 were made in the dry state and a load up to 2000 lbs. was applied, the maximum load permissible due to the heating of the machine. In these tests no measure of wear could be made on the control test pieces which could not withstand a load of 1250 lbs. Likewise, no measure of wear could be made on Sample No. 4 (cast iron) treated in bath N due to rapid jamming of the sample in the jaws of the apparatus.

In the following tables, all the weights are indicated in grams. The value indicated as "degree of wear" is the difference between the initial weight of the test piece and its final weight after the test.

TABLE IV

(Sample No. 1)

Treatment in bath	"N"	"S_1"	"S_2"	"S_3"	"S_4"
Initial weight	8,110	8,108	7,932	7,965	8,013
Final weight	7,786	8,094	7,921	7,950	7,936
Degree of wear	0.324	0.014	0.100	0.015	0.017

Duration of the tests: For the test piece treated in bath "N," the test was interrupted after 4 minutes and 10 seconds due to jamming. For the test pieces treated in baths "S_1," "S_2," "S_3" and "S_4" the test lasted 10 minutes.

TABLE V

(Sample No. 2)

Treatment in bath	"N"	"S_1"	"S_2"	"S_3"	"S_4"
Initial weight	7,396	7,525	7,398	7,450	7,600
Final weight	5,849	7,523	7,396	7,431	7,584
Degree of wear	1,547	0.002	0.002	0.019	0.016

Duration of the tests: 10 minutes for all the test pieces.

TABLE VI

(Sample No. 3)

Treatment in bath	"N"	"S_1"	"S_2"	"S_3"	"S_4"
Initial weight	7,545	7,527	7,048	7,432	7,565
Final weight	7,487	7,522	7,042	7,426	7,558
Degree of wear	0.058	0.005	0.006	0.006	0.007
Duration of the test	3' 30"	4' 30"	4 min.	4 min.	4' 30"
Final load	1,750 [1]	2,000 [2]	2,000 [2]	2,000 [2]	2,000 [2]

[1] Limited through jamming.
[2] No jamming.
The test pieces treated in the baths "S_1," "S_2," "S_3," and "S_4" were rotated until frication caused the pieces to heat to red heat, yet there was no jamming.

TABLE VII

(Sample No. 4)

Treatment in bath	"N"	"S_1"	"S_2"	"S_3"	"S_4"
Initial weight	7,530	7,321	7,645	7,128	6,940
Final weight	(1)	7,309	7,623	7,109	6,919
Degree of wear	(1)	0,012	0.013	0.017	0.021

[1] Measure impossible.
Duration of the tests: The reference or control test piece broke 30 sec. after application of a load of 1,250 lbs. The test piece treated in bath "N" broke immediately after application of a load of 2,150 lbs. The test pieces treated in baths "S_1," "S_2," "S_3," "S_4" rotated for 10 minutes without jamming.

The foregoing measures of wear demonstrate that ferrous metal pieces treated according to this invention possess extraordinary resistance to wear.

The fact that these improved results are due to the introduction of the sulfur into the surface of the treated pieces is confirmed further by the chemical tests which are reported hereinafter. These tests also show that the depth of penetration of the sulfur, i. e. the thickness of the treated layer, depends upon the duration of the treatment.

A cylindrical test piece of 26 mms. diameter was machined from the above mentioned steel Sample No. 3 and treated, according to the invention, in Bath "S_2" for 160 minutes at a temperature of 580° C.

This test piece was weighed and then introduced into a suitable apparatus such as Strohlein apparatus where it was attacked by hydrochloric acid. The escaping gases were dissolved in the following solution:

Zinc acetate	25 grams.
Cadmium acetate	5 grams.
Acetic acid	200 ccm.
Water	balance to 1000 ccm.

The attack was stopped after a desired recorded peroid of time and the test piece was weighed again. Then the solution containing the dissolved gases was quantitatively analyzed for its sulfur content by means of an N/10 solution of iodine and of an N/10 solution of thiosulfate in the presence of starch dressing. The weight difference of the test piece between the beginning and the end of the attack made it possible to calculate the thickness of the layer destroyed by the attack.

Through repeating the same operation several times it was possible to determine the variation in the quantity of sulfur in the various layers dissolved from test pieces. The results of this test are illustrated by the curve of the accompanying Figure 1 showing the variations in the quantity of sulfur present at different distances from the surface of the test piece made from ferrous alloy Sample No. 3 after being treated in Bath "S_2" for 60 minutes at 580° C. From the curve it is clear that the percentage of sulfur present decreases as the thickness of the layer increases.

In another test, a plurality of cylindrical test pieces of 26 mm. diameter in which an axial bore of 10 mm. had been made were also treated in the same Bath "S_2" at a temperature of 580° C. for varying periods of time. After treatment, the pieces were subjected to the Baumann test. This test consisted in machining flat and roughly polishing one of the ends of each test piece and then applying the polished surface to a sensitized photographic paper on which a 5% solution of hydrochloric acid had previously been spread. After a few minutes, two concentric brown rings or halations were formed on the paper, corresponding to tracings of the internal and external surface layers formed on the test piece. It is known that this brown coloration in the test of Baumann denotes the presence of sulfur.

The thickness of the halations or rings was measured with precision and it was found that this thickness was the greater, the longer the duration of the treatment according to this invention. This thickness, which was of about several hundredths of one millimeter for a treatment lasting 20 minutes, reached 0.3 mm. after a treatment of 180 minutes.

Finally, in order to check the thickness of the wear resisting layer obtained according to this invention, the following test was performed.

A number of test pieces of 6.35 mm. diameter were made from ferrous metals of the same composition as Samples No. 3 and No. 4. The test pieces made from the respective metals were treated in accordance with this invention in Bath S_2 for different periods of time. After treatment, the test pieces were subjected to wear tests in the Faville-Levally apparatus under the previously described conditions for a given time. Then the tested piece was ground or machined a desired amount and again subjected to the same wear test during the same period of time and so on. A reference or control test piece was kept untreated for each sample and subjected to the same wear and machining tests for camparative purposes.

In measuring the wear resistance of the control or untreated test pieces it was found that the wear was substantially uniform, while in measuring the wear resistance of the treated test pieces it was found that the extent of the wear suddenly increased between two successive wear tests, passing from a comparatively small value to a value which was substantially equal to the wear on the control test pieces. It was thus possible by observing the sudden increase in wear on the treated test pieces to determine for each test piece the thickness of its wear resistant layer.

To illustrate, one of the test pieces, made of the composition of Sample No. 4 and treated in Bath S2, showed the following results:

TABLE III

Pass No.	Initial diameter (millimeters)	Degree of wear (milligrams) after a test of 10 minutes.
1	6.35	4
2	6.25	5
3	6.15	5
4	6.05	6
5	5.95	11
6	5.75	119

At the moment of the sixth pass through the testing machine the degree of wear was substantially the same as that of the reference or control test piece. It was therefore possible to conclude that at the moment of the fifth pass the wear resisting layer obtained according to the invention had been removed completely through grinding. The depth of said layer was, therefore, between 0.3 and 0.4 mm.

Curves A and B in Figure II of the accompanying drawing record the results obtained by applying the tests described immediately above to the several test pieces of the compositions of Sample No. 3 and Sample No. 4 respectively.

This application is a continuation-in-part of our application Serial No. 2,333, filed January 14, 1948, now abandoned.

It will be understood that the foregoing detailed description and examples constitute illustrative embodiments of our invention and that various modifications and changes can be made therein without departing from the spirit of our invention or the scope of the appended claims.

We claim:

1. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises subjecting a surface of the metal piece to the action of a molten alkaline salt composition having a temperature above 550° C. and containing a molten sulfur salt in which the sulfur is incompletely oxidized in an amount sufficient to incorporate sulfur into the ferrous metal, until the ferrous metal contains added sulfur to a depth of more than .05 mm. from said surface.

2. A salt bath composition for surface treating ferrous metal pieces consisting essentially of alkali metal sulfur salt containing sulfur in an incompletely oxidized state, alkali metal cyanide, alkali metal cyanate, and diluent salt consisting essentially of alkali metal carbonate and alkali metal chloride, the content of such sulfur being about 0.4 to 2 per cent and the contents of cyanide and cyanate being at least about 25 per cent of the weight of the composition, the diluent salt being the predominant constituent.

3. A wear resistant ferrous metal article comprising a piece of ferrous metal containing added sulfur in a chemically combined state in an integral part of the ferrous metal extending from the surface thereof to a depth of more than .05 mm. in the body thereof, produced by the process described in claim 1.

4. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises subjecting a surface of the metal piece to the action of a molten salt composition having a temperature above 550° C. and containing an alkali metal sulfur salt in which the sulfur is incompletely oxidized in an amount sufficient to incorporate sulfur into the ferrous metal, until the ferrous metal contains added sulfur to a depth of more than .05 mm. from said surface.

5. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises subjecting a surface of the metal piece to the action of a molten salt composition having a temperature above 550° C. and containing a molten alkali metal sulfur salt comprising incompletely oxidized sulfur, said composition containing about 0.4 to 2% by weight of such sulfur, until the ferrous metal contains added sulfur to a depth of more than .05 mm. from said surface.

6. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises subjecting a surface of the metal piece under reducing conditions to the action of a molten salt composition having a temperature above 550° C. and containing at least one molten alkali metal sulfur salt from the group consisting of alkali metal sulfides, sulfites, thiosulfates, sulfocyanates and thiourea salts in an amount sufficient to incorporate sulfur into the ferrous metal, until the ferrous metal contains added sulfur to a depth of more than .05 mm. from said surface.

7. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises subjecting a surface of the metal piece to the action of a molten salt composition having a temperature above 550° C. and containing at least one alkali metal sulfur salt in which the sulfur is incompletely oxidized and at least one alkali metal cyano salt from the group consisting of alkali metal cyanides and alkali metal cyanates in amounts sufficient to incorporate sulfur into the ferrous metal, until the ferrous metal contains added sulfur to a depth of more than .05 mm. from said surface.

8. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises subjecting a surface of the metal piece to the action of a molten salt composition having a temperature above 550° C. and containing a molten alkali metal sulfide in an amount sufficient to incorporate sulfur into the ferrous metal, until the ferrous metal contains added sulfur to a depth of more than .05 mm. from said surface.

9. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises subjecting a surface of the metal piece to the action of a molten salt composition having a temperature above 550° C. and containing a molten alkali metal sulfide and a molten alkali metal cyanate in amounts sufficient to incorporate sulfur into the ferrous metal, until the ferrous metal contains added sulfur to a depth of more than .05 mm. from said surface.

10. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises subjecting a surface of the metal piece to the action of a molten salt composition having a temperature above 550° C. and containing a molten alkali metal sulfide and a molten alkali metal sulfocyanate in amounts sufficient to incorporate sulfur into the ferrous metal, until the ferrous metal contains added sulfur to a depth of more than .05 mm. from said surface.

11. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises immersing and holding a surface of the metal piece in a molten salt composition having a temperature above 500° C. and possessing reducing properties and containing in molten state at least one alkali metal sulfur salt in which the sulfur is incompletely oxidized and at least one alkali metal cyano salt from the group consisting of alkali metal cyanides and alkali metal cyanates in amounts sufficient to incorporate sulfur into the ferrous metal, until the ferrous metal contains added sulfur to a depth of more than .05 mm. from said surface.

12. The process of producing a surface having enhanced gear resistance on a piece of ferrous metal, which comprises immersing and holding a surface of the ferrous metal piece in a molten salt composition having a temperature above 500° C. and possessing reducing properties and containing in molten state an alkali metal sulfide and an alkali metal cyanide in amounts sufficient to incorporate sulfur into the ferrous metal, until the ferrous metal contains added sulfur to a depth of more than .05 mm. from said surface.

13. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises immersing and holding a surface of the ferrous metal piece in a molten salt composition having a temperature above 500° C. and possessing reducing properties and containing in molten state an alkali metal sulfide, an alkali metal cyanide and an alkali metal cyanate in amounts sufficient to incorporate sulfur into the ferrous metal, until the ferrous metal contains added sulfur to a depth of more than .05 mm. from said surface.

14. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises immersing and holding a surface of the ferrous metal piece in a molten salt composition having a temperature above 500° C. and possessing reducing properties and containing in molten state an alkali metal sul-

fide, an alkali metal sulfocyanate, an alkali metal cyanide and an alkali metal cyanate in amounts sufficient to incorporate sulfur into the ferrous metal.

15. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises immersing and holding a surface of the ferrous metal piece in a molten mixture of salts at a temperature above 550° C., said mixture containing in molten state an alkali metal sulfide, an alkali metal sulfocyanate, an alkali metal cyanide and an alkali metal cyanate in amounts sufficient to incorporate sulfur into the ferrous metal.

16. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises immersing and holding a surface of the ferrous metal piece in a molten mixture of salts at a temperature above 550° C., said mixture containing in molten state an alkali metal sulfide, an alkali metal sulfocyanate, an alkali metal cyanide and an alkali metal cyanate, said salts containing incompletely oxidized sulfur in an amount between about 0.4 and 2 per cent of the weight of the mixture.

17. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises immersing and holding a surface of the ferrous metal piece in a molten mixture of salts at a temperature of the order of 550° to 600° C., said mixture containing in molten state an alkali metal sulfide, an alkali metal sulfocyanate, an alkali metal cyanide and an alkali metal cyanate and having reducing properties, said salts containing incompletely oxidized sulfur in an amount between about 0.4 and 2 per cent of the weight of said mixture.

18. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises melting together salts including an alkali metal cyanide and an alkali metal sulfur salt in which the sulfur is incompletely oxidized to form a salt bath that is molten at a temperature of 550° C., said salts comprising at least about 25 per cent by weight of cyano salt and from about 0.4 to 2 per cent by weight of incompletely oxidized sulfur, and immersing and holding a surface of the ferrous metal piece in the molten bath at a temperature of the order of 550° to 600° C.

19. The process of producing a surface having enhanced wear resistance on a piece of ferrous metal, which comprises melting together salts including an alkali metal cyanide, an alkali metal sulfur salt in which the sulfur is incompletely oxidized and a major proportion of diluent salt to form a salt bath that is molten at a temperature of 500° C., said salts containing from about 0.4 to 2 per cent by weight of incompletely oxidized sulfur, and immersing and holding a surface of the ferrous metal piece in the molten bath at a temperature of the order of 550° to 600° C.

20. A salt composition for surface treating ferrous metal pieces comprising in admixture at least one alkali metal sulfur salt in which the sulfure is in an incompletely oxidized state, a larger proportion of alkali metal cyano salt selected from the group consisting of alkali metal cyanides and alkali metal cyanates, and at least one alkaline diluent salt forming a major proportion of the mixture, the mixture being molten at a temperature of 550° C. and said salts containing from about 0.4 to 2 per cent by weight of incompletely oxidized sulfur.

21. A salt bath composition for imparting wear resistance to ferrous metal articles consisting essentially of a mixture of alkaline salts containing from 0.4 to 2% by weight of sulfur in a chemically combined but incompletely oxidized state and melting at a temperature below 500° C., said salts including at least one alkali metal sulfur salt from the group consisting of alkali metal sulfides, sulfites, thiosulfites, sulfocyanates and thiourea salts and at least one alkali metal cyano salt from the group consisting of alkali metal cyanides and cyanates, said mixture containing a larger proportion of such cyano salt than of such sulfur salt and alkaline diluent salts being its predominant constituent.

22. A salt bath composition for imparting wear resistance to ferrous metal articles, consisting essentially of a mixture of salts that is molten at a temperature of 550° C. and contains from 0.4 to 2% by weight of sulfur in a chemically combined but incompletely oxidized state, said salts including an alkali metal sulfide, an alkali metal cyanide, an alkali metal cyanate and a major proportion of alkaline diluent salts.

23. A salt bath composition for imparting wear resistance to ferrous metal pieces, consisting essentially of a mixture of alkaline salts that is molten at a temperature of 550° C. and contains from 0.4 to 2% by weight of sulfide sulfur, said mixture in molten state containing an alkali metal sulfocyanate, an alkali metal sulfide, an alkali metal cyanide and an alkali metal cyanate.

24. A salt bath composition for imparting wear resistance to ferrous metal pieces, consisting essentially of a mixture of alkaline salts including an alkali metal sulfite and an alkali metal cyanide, said salts containing from about 0.4 to 2% by weight of incompletely oxidized sulfur and said mixture being molten at a temperature of 550° C.

25. A salt bath composition for imparting wear resistance to ferrous metal pieces, consisting essentially of a mixture of alkaline salts including an alkali metal thiosulfate and an alkali metal cyanide, said salts containing from about 0.4 to 2% by weight of incompletely oxidized sulfur and said mixture being molten at a temperature of 550° C.

26. A salt bath composition for imparting wear resistance to ferrous metal pieces, consisting essentially of a mixture of alkaline salts including an alkali metal sulfide and an alkali metal cyanate, said salts containing from about 0.4 to 2% by weight of incompletely oxidized sulfur and said mixture being molten at a temperature of 550° C.

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