

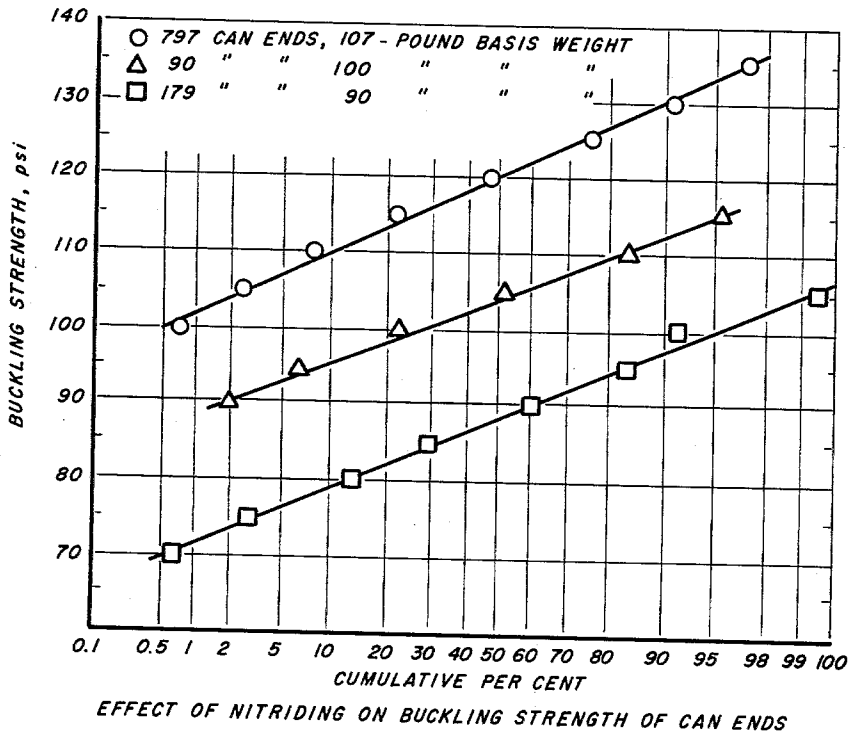
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H. E. HARTNER ETAL

3,219,494

METHOD OF MAKING HIGH-STRENGTH TIN PLATE

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INVENTORS
HOWARD E. HARTNER and
ANDREW LESNEY

By *Donald H. Dalton*
Attorney

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3,219,494
METHOD OF MAKING HIGH-STRENGTH
TIN PLATE

Howard E. Hartner, Pittsburgh, and Andrew Lesney,
Frazer Township, Allegheny County, Pa., assignors to
United States Steel Corporation, a corporation of New
Jersey

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2 Claims. (Cl. 148-16)

This application is a continuation-in-part of our co-
pending application, Serial No. 112,075, filed May 23,
1961, now abandoned.

This invention relates generally to nitrogen additions
to steel, and more particularly, to adding nitrogen to a
strip of steel and diffusing the added nitrogen through
the steel.

The conventional method of producing high nitrogen
steel (above 0.010% N) is by ladle or mold additions of
calcium cyanamid or similar nitrogen-bearing com-
pounds. This method of adding nitrogen to the steel
while it is in the molten state has several disadvantages.
Such nitrogen-bearing compounds are expensive, the ni-
trogen recovery by the steel varies widely, smoke and
fumes create a safety hazard, and rolling of high nitrogen
steel is difficult with yield being comparatively low.

It is therefore a principal object of this invention to
add nitrogen to steel while the steel is in the solid state.

A related object of this invention is to add nitrogen to
steel after it has been rolled to a strip.

Yet another object of this invention is to provide a
method of closely controlling the amount of nitrogen
added to steel.

A more particular object of this invention is to use am-
monia gas as an agent to introduce nitrogen into steel,
and thereafter cause uniform diffusion of the added ni-
trogen through the steel.

Other objects will appear, and a fuller understanding
of the invention may be had by reference to the follow-
ing specification and attached drawing.

The drawing is a graph showing the buckling strength
of can ends formed from steel made according to this
invention.

It has been found that if a steel strip is nitrified to
produce a nitrogen-rich outer case, and thereafter heated
to a temperature above the recrystallization temperature
of the steel in an atmosphere free of nitriding agents, the
nitrogen will diffuse through the strip and a steel of su-
perior strength properties is produced.

This method of forming a high strength steel has par-
ticular application in, though not limited to, the manu-
facture of steel for tin plate, so the description will be of
the process as it is applied to such coils of steel. One
or more opened coils are placed in a furnace. This type
of coil and how it is produced are described in an article
in "Industrial Heating," May 1958, p. 949. The com-
position range for a typical steel suitable for the method
of this invention is given in Table I below. This is a
conventional range for steel suitable for electrolytic tin
plating. However, this range is illustrative only, and
any steel which can be nitrified and the nitrogen diffused

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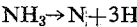
through the steel uniformly can be treated according to
this invention.

Table I

Component:	Percent by weight
C	0.04 to 0.20
Mn	0.25 to 0.75
P	0.012 max.
S	0.040 max.
Si	0.010 max.
Cu	0.13 max.
Ni	0.10 max.
Cr*	0.06 max.
Mo*	0.05 max.
Fe and residual impurities*	Bal.

*The nitrogen content is about 0.003%, and in this type of
steel can be considered a residual impurity; the Cr and Mo
contents are residual amounts and hence, this steel is substan-
tially free of strong nitride formers.

A cover is placed on the furnace and the coil or coils
in the furnace are heated. Ammonia gas is introduced
into the furnace at this early point in the heating cycle.
Upon heating, the ammonia gas produces the nitrogen
needed for nitriding by the following reaction:



The hot surface of the steel acts as a catalyst to decom-
pose the ammonia and a portion of atomic nitro-
gen coming into contact with the surface is absorbed
into the surface of the steel forming a nitrogen-rich outer
case. The remainder of the atomic nitrogen reacts to
form N_2 . The heating of the coils continues and the
ammonia atmosphere is maintained until the desired
amount of nitrogen is absorbed into the case. Producing
this type of nitride case on steel is well known in the
art. It is also known that different concentrations of
ammonia gas and different temperatures, and the time the
steel is maintained in a nitriding atmosphere affect the
amount of nitrogen absorbed in the case and the depth
of the case. Relatively simple experimentation will indi-
cate the specific times, heating rates (i.e. temperatures)
and concentrations of ammonia gas needed to provide a
given percentage of nitrogen in the steel. It has been
found generally that in adding between 0.015% and
0.15% nitrogen to steel by this method that the increase
of nitrogen percentage is directly dependent upon the
time, temperature, and concentration of the ammonia
gas.

The nitride case produced by this initial step is hard
and brittle. Subsequent operations performed on a strip
having a nitrified case tend to crack the steel. Further,
this case does not impart much, if any, additional strength
to the steel. Hence, it has been found to be necessary
to diffuse the nitrogen from the case substantially uni-
formly through the steel.

To accomplish this diffusion the ammonia gas is purged
from the furnace while the steel coils are continued to be
heated by introducing a gas free of nitriding agents into
the furnace. Conventional inert atmosphere gases, such
as 5% H_2 and 95% N_2 , can be used. The coils are heated
in this atmosphere gas which is free of nitriding agents
to above the recrystallization temperature of the steel and
given a short soak. This heating to a temperature above
the recrystallization temperature of the steel causes the
nitrogen to diffuse from the nitrogen-rich case uniformly

throughout the steel. This uniform diffusion is a diffusion of the nitrogen from the case to the core below the case. There may be some variation of the amount of nitrogen in the case at different locations on the strip. Hence, uniform as used herein means uniform through an entire cross section at any given location on the strip.

It has been found that for coils of steel to be tin plated, which steels are substantially free of strong nitride formers such as Cr, Mo and Al (i.e. there is substantially no detectable acid soluble Al and no more than about .05% Mo and .06% Cr and the total amount of strong nitride formers is less than .5%) that heating between 1050° F. and 1150° F. and holding at this temperature for one-half to three-quarters of an hour is optimum, although temperatures between 1000° F. and 1350° F. would be satisfactory. For other types of steel the optimum temperature ranges and time may vary but in all instances it is necessary to heat above the recrystallization temperature of the steel. The heating, from the beginning, is continuous since commercially this is desired. However, it is necessary only to first form a nitrogen-rich case, and then cause diffusion of the nitrogen from the case uniformly throughout the steel. Hence, the invention could be practiced in two separate steps without continuously heating the coils. For example, the coils could be held at a nitriding temperature for a period of time, and then heated to above the recrystallization temperature.

After the nitrogen has been diffused through the steel, the coils are cooled. The resulting structure is a high nitrogen steel which has excellent strength and does not have a hard or brittle case. The coils are then electrolytically plated with tin in a conventional manner.

Several tests were performed on can ends and test strips formed from coils of the composition of Table I and having nitrogen added and diffused according to this invention. The nitrogen content varied between 0.012% and 0.051%. Ninety tensile tests were made on steel from coils having a 107 pound basis weight. The tests showed a minimum tensile strength of 67,000 p.s.i. and a maximum of 117,400 p.s.i., with the median being about 79,000 p.s.i. Ten tensile tests were made on steel from coils having a 100 pound basis weight. The tests showed a minimum tensile strength of 71,000 p.s.i. and a maximum of 75,500 p.s.i., with the median being about 74,000 p.s.i. Twenty tensile tests were made on the steel from coils having 90 pound basis weight. The tests showed a minimum tensile strength of 63,700 p.s.i. and a maximum of 76,500 p.s.i., with the median being about 71,800 p.s.i.

Tests for buckling strength were performed on can ends formed from coils having the above basis weights. The cumulative percentages of the number of ends having buckling strength lower than a given value is indicated in the graph. This graph indicates that less than 1% of the ends formed from 107 pound basis weight coils had a buckling strength of less than 100 p.s.i. and that only 2% of the ends formed from coils having a 100 pound basis weight had a buckling strength of less than 90 p.s.i.

The above tensile strength and buckling strength values are much higher than any obtainable with the strip before nitriding and diffusing according to this invention. In fact these values compare favorably with those of high phosphorous steel which has been the conventional material used for beer-can-end application.

Metallographic examination of the resulting steel indicates that much of the nitrogen is in solid solution in ferrite. That which is not in solution has precipitated out as iron-nitride needles, Fe_{16}N_2 and Fe_4N . The Fe_{16}N_2 needles are so small that they can be seen only with magnification obtainable with electron microscopes.

One of the outstanding advantages of this invention is the minimum change required in the normal annealing cycle. Conventional furnaces are used needing no modifications. During the early part of the cycle ammonia is substituted for conventional inert atmosphere gas. It may be necessary to modify slightly the heating rate of annealing temperature to obtain the desired percentage of nitrogen in the case. However, once this case has been attained, the NH_3 is urged and the remainder of the annealing cycle is conventional including the use of conventional inert atmosphere gases. Ammonia gas is relatively inexpensive so there is no appreciable cost increase over normal annealing operations. Also, the nitrogen has been added to the steel after it has been rolled to the desired gage. Thus, difficulties encountered in rolling steel with high nitrogen content are eliminated. Closer control of the nitrogen content is possible than by ladle or mold additions, and no noxious fumes are admitted to the atmosphere.

Although one form of our invention has been described it will be apparent that other adaptations and modifications may be made without departing from the scope of the following claims.

We claim:

1. The method of making high-nitrogen steel strip for high-strength tin plate and the like, comprising:
 - (a) nitriding, after rolling, steel strip containing less than about 0.5% of strong nitride formers and no more than a residual amount of nitrogen, until a nitrogen-rich case is produced thereon which provides an average nitrogen content for the strip cross-section as a whole of above about 0.010%; and
 - (b) diffusing the nitrogen of said nitrogen-rich case substantially uniformly throughout the strip cross-section to obtain a high-strength high-nitrogen core, which does not have a hard case, said nitrogen diffusion being accomplished by annealing the strip at a temperature above its recrystallization temperature in an inert atmosphere.
2. The method of making high-nitrogen steel strip for high-strength tin plate and the like, comprising:
 - (a) nitriding, after rolling, steel strip containing less than about 0.5% of strong nitride formers and no more than a residual amount of nitrogen, until a nitrogen-rich case is produced thereon which provides an average nitrogen content for the strip cross-section as a whole of above about 0.010%, said nitriding being accomplished by heating the strip in opened coil form in an atmosphere of NH_3 ; and
 - (b) diffusing the nitrogen of said nitrogen-rich case substantially uniformly throughout the strip cross-section to obtain a high-strength high-nitrogen core, which does not have a hard case, said nitrogen diffusion being accomplished by annealing the strip in opened coil form at between 1000° F. and 1350° F. in an inert atmosphere.

References Cited by the Examiner

UNITED STATES PATENTS

1,774,999	9/1930	Sergeson	148—16.6
2,592,282	4/1952	Hodil	148—16
2,594,129	4/1952	Crego	148—16
3,058,856	10/1962	Miller	148—16

FOREIGN PATENTS

522,252	6/1940	Great Britain.
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BENJAMIN HENKIN, *Primary Examiner.*

WINSTON A. DOUGLAS, DAVID L. RECK,
Examiners.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,219,494

November 23, 1965

Howard E. Hartner et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 6, for "of" read -- to --; line 9, for "urged" read -- purged --.

Signed and sealed this 27th day of September 1966.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents