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W. H. PHILLIPS

FERROUS BASE ARTICLE OF MANUFACTURE

Original Filed April 14, 1927

2 Sheets-Sheet 1

Fig. 1.

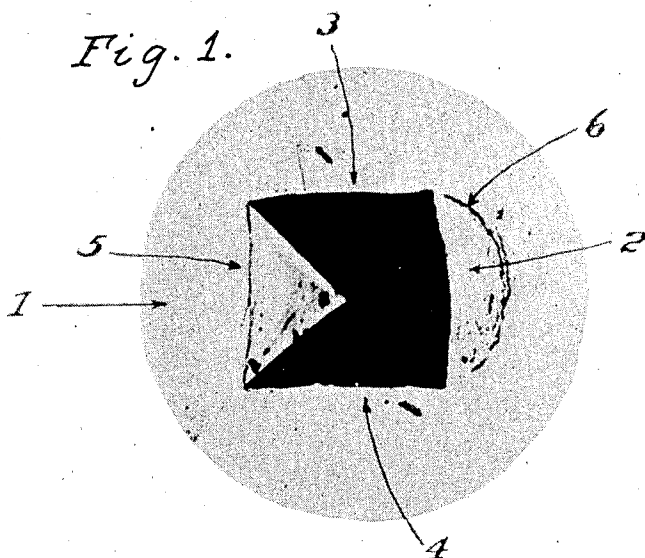


Fig. 2.



WITNESSES

ABW allcock
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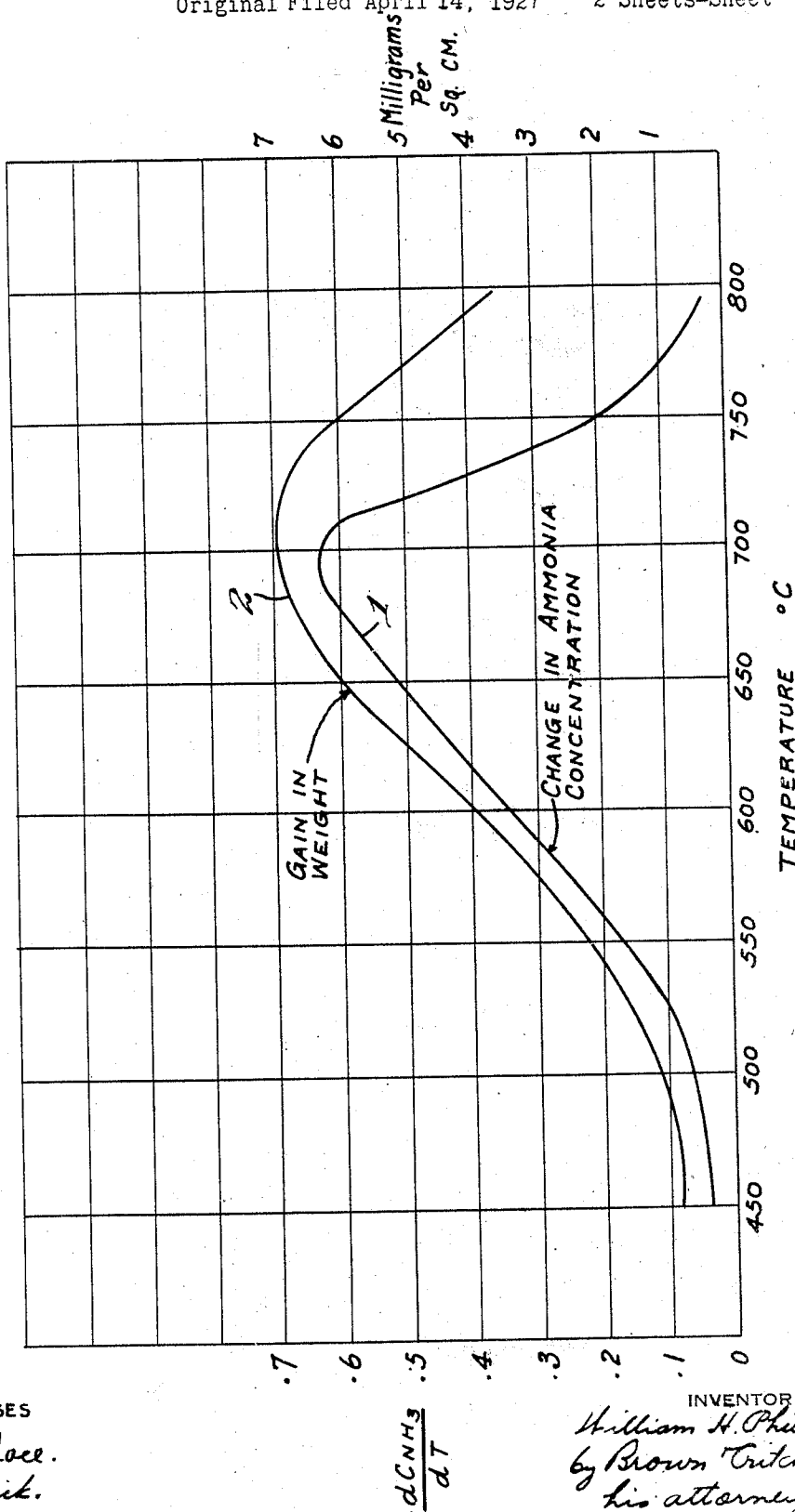


Fig. 3.

WITNESSES

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$\frac{dC_{NH_3}}{dT}$

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UNITED STATES PATENT OFFICE.

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FERROUS BASE ARTICLE OF MANUFACTURE.

Continuation of application Serial No. 183,910, filed April 14, 1927. This application filed July 13, 1928. Serial No. 292,407.

This application is a continuation of my pending application Serial No. 183,910, filed April 14, 1927.

In the accompanying drawings, to which reference will later be made, Fig. 1 is a photomicrograph of a tough nitrogenated case; Fig. 2 a photomicrograph of a brittle nitrogenated case; and Fig. 3 curves plotted from data obtained in the nitrogenation of a certain steel.

The phenomena of surface nitrogenation of iron and steel, to which this invention pertains, were extensively investigated by Fry, as shown in his article in *Stahl und Eisen*, 43, 1271 (1923), according to which he found, among other things, that by subjecting plain carbon steel to ammonia at an elevated temperature there is formed on the surface of the steel a very hard and extremely brittle iron nitride layer composed largely of what he termed the higher and lower iron nitrides, Fe_3N and Fe_4N . He also found that in some instances thicker and harder iron nitride layers are similarly formed on the surface of low carbon alloy steels containing chromium, titanium, aluminum, manganese, vanadium and silicon.

In research and commercial development work heretofore done on the nitrogenation of steel, the best results, from commercial and practical standpoints, have been obtained by the use of relatively low carbon alloy steels containing aluminum and chromium. However, the nitrogenation of these steels is attended by serious disadvantages both with respect to procedure and to the resulting product. As to procedure, it requires the exposure of an article formed of aluminum-chromium alloy steel to an atmosphere containing nitrogen, derived from the introduction of ammonia into a furnace containing the article, at a temperature of about $540^{\circ}C$. for a period of fifty or more hours to form on the steel a case about one-thirty-second of an inch in thickness. As to the product resulting from the nitrogenation of aluminum-chromium steels, the layers termed "iron nitride" by Fry have satisfactory hardness and thickness, but they are deficient in toughness and cohesiveness. These disadvantages, procedural, economic and physical, incident to

the surface hardening of steel by the nitrogenation process, have greatly deterred the commercialization of the process, and have proportionately deprived the industries of the advantages inherent in iron and steel articles provided with satisfactory nitrogenated surface layers or cases.

The objects of this invention are to produce ferrous base articles of manufacture having surface layers or cases produced by nitrogenation which firmly adhere to the main body of the article, which in addition to being hard are also tough, cohesive, and resistant to corrosion, and which articles may be produced at less cost than prevailed prior to my invention.

Previous disclosures in this art appear to have drawn distinctions between various types of ferrous materials adapted for nitrogenation. My invention is, on the contrary, applicable to all types of ferrous material, whether iron or steel, and whether cast, wrought or heat treated in any manner used in the production of ferrous articles. In the specification and claims the term "ferrous base" is used for purposes of description as comprehending all these materials in their various conditions.

The invention is predicated primarily upon my discovery that its stated objects may be attained by alloying molybdenum in substantial amount with the ferrous base used in the manufacture of articles which are to be surface hardened by nitrogenation processes. I have discovered that an article formed of steel containing molybdenum as an essential alloying element may be provided with a hard, adherent, tough cohesive and corrosion-resistant layer or case of satisfactory thickness by subjecting it to nitrogenation at an elevated temperature for a period of time less than half, and in some cases less than a fifth of that heretofore considered necessary for nitrogenation of articles made of the steels heretofore considered best suited for the purpose.

As just used, and as further used herein and in the appended claims with reference to nitrogenated cases the term "toughness" defines that physical characteristic of the material of the case which enables it to undergo

plastic flow with little or no spalling in the immediate vicinity of an indentation in the case formed by the Vickers diamond indenter hardness tester. Similarly, the term "brittleness" is used herein to define that physical characteristic of the case which prevents it from undergoing plastic deformation and instead causes it to spall in the immediate vicinity of an indentation of the type just referred to. Also, as applied to the cases produced in accordance with the invention, the term "cohesiveness" describes the ability of each differential physical unit of the case material to cling to neighboring differential physical units.

These terms may be further understood and the benefits of the invention shown in part by reference to Figs. 1 and 2. Fig. 1 illustrates a tough case formed by nitrogenation of a steel containing molybdenum in accordance with the invention, but not containing chromium. Fig. 2 illustrates a brittle nitrogenated case on a chromium steel containing no molybdenum.

After nitrogenation, one surface of these samples was ground on a taper of one to twenty. The grinding was carried out slowly under a heavy air blast to retain the structure of the metal in an unchanged condition. Hardness measurements were then made on these ground faces, beginning at the outer surface of the case, using a Vickers diamond indenter hardness tester.

The surface surrounding Fig. 2 was located about 0.004 inch below the outer nitrogenated surface. It will be observed that the material of the case was not capable of undergoing plastic flow as thus indented, but instead spalled severely. The outer four-thousandths of the case was all found to be brittle, and the first tough material was found just below the region of Fig. 2. The hardness at this latter point, as measured by the Vickers machine, was about 1000 Brinell.

The surface surrounding the indentation shown in Fig. 1, and characteristic of the tough cases produced by the invention, was located about 0.0005 inch below the outer surface of the specimen as nitrogenated, and the hardness was about 1000 Brinell. It will be noted that the indentation is clear and sharp, and that the material of the case has been plastically deformed without spalling.

This specimen was illuminated in the direction of the arrow 1. The material in the region 2 shows plastic flow. The apparent lack of plastic flow in regions 3, 4 and 5 is due to the type of illumination used in photographing the specimen and the shape of the material as piled up by plastic flow. Examination under the microscope showed that plastic flow had actually taken place on all four sides of the indentation. The curved, dark lines 6 are not cracks, but are actually shadows cast by the plastically flowed mate-

rial. This was proved by rotation of the specimen under the microscope upon which the lines disappeared.

The hardness tester referred to is preferred because of its ability to distinguish between tough and brittle nitrogenated cases. The Herbert pendulum hardness tester reveals no material difference in hardness between these two specimens at the locations of Figs. 1 and 2. The difference in quality between these two cases, however, is vital from the standpoint of abrasive wear; and the differences shown bears out the proven principle that resistance to abrasive wear is best secured by a combination of hardness and toughness.

It is my belief that the nitrogenation of ferrous materials heretofore nitrogenized required long periods of time because the products of their nitrogenation are stable and form with difficulty, even in the presence of nascent nitrogen, such as that resulting from the dissociation of ammonia in the presence of the article being treated; and also because such products either diffuse very sluggishly, or are so stable that the nitrogen sluggishly diffuses from them.

I have discovered that the addition of molybdenum to the ferrous base so accelerates or activates the nitrogenation process as to give more satisfactory results than heretofore obtained, and in less time than was formerly considered necessary. My observation of these nitrogenated articles leads me to believe that the beneficial action of molybdenum in the nitrogenation process is due to its unique property of readily forming nitrides which dissociate readily according to a reversible reaction, whereby, in the ferrous base, molybdenum becomes an internal transferer of active nitrogen. Thus the molybdenum acts as an energetic nitrogen collector, transferring nitrogen in a form in which it can be distributed at a rate and in a condition such that it is readily assimilable by the metal, perhaps as an easily diffusible nitride, or as nitrogen in a particularly reactive or diffusible state. Molybdenum may, and probably does, contribute to the hardness in other ways, as by increasing the hardness of the iron by forming additional solid solutions which go hand in hand with increased hardness.

In addition to containing molybdenum as an essential alloying element, the ferrous base of which the articles are formed may also contain other alloying elements for producing hardness, strength or other desired characteristics in the product; and it may, and usually does, contain the usual elements present as impurities and as incidental to commercial processes of manufacture of iron or steel. In articles formed of steel, which embody the preferred form of this invention, the steel preferably contains aluminum or

its equivalent. When an article provided according to this invention is formed of steel containing aluminum as well as molybdenum, the steel may contain carbon up to about 1 per cent, molybdenum from about 0.1 up to about 4 per cent, and aluminum from about 0.1 up to about 4 per cent. A typical analysis of steel found to be particularly suitable comprises:

- Aluminum—from about 2 to about 3%.
Carbon—from about 0.25 to about 0.35%.
Manganese—from about 0.50 to about 0.90%.
Molybdenum—from about 0.75 to about 1.00%.
Silicon—from about 0.20 to about 0.25%.
Phosphorus—not over about 0.04%.
Sulphur—not over about 0.04%.

The manganese and silicon contents of this typical analysis are those customarily found in steel as incidental to its manufacture, and the percentages of phosphorus and sulphur are normal.

As a specific example of the invention, an article formed of steel containing:

- Aluminum----- 2.2 %
Carbon----- 0.29%
Manganese----- 0.55%
Molybdenum----- 0.89%
Silicon----- 0.18%
Phosphorus----- below 0.04%
Sulphur----- below 0.04%

was subjected to nitrogenation by exposure to ammonia in a closed chamber at a temperature of about 540° C. After ten hours' treatment it was found to have a satisfactory nitrogenated surface layer. The layer adhered very firmly to the main body of the steel, and was very hard. It was also quite tough and cohesive in comparison with the surface layers heretofore produced by nitrogenation.

As a further specific example, an article made of cast iron containing 3.5 per cent of carbon and 0.60 per cent of molybdenum after being subjected to nitrogen at a temperature of 540° C. for a period of twenty hours, was found to have a satisfactorily hardened surface layer.

The foregoing examples of nitrogenation according to the invention illustrate the benefits to be obtained by the addition of molybdenum as an alloying element. In order to obtain a case of the same depth without the use of molybdenum, the steel would have to be subjected to nitrogenation for a much longer period. My experiments indicate that as the nitrogenation of any steel by heating in ammonia is prolonged, the surface starts on a transition from a tough toward a brittle condition. Thus, processes requiring long exposure are not only expensive, but tend to produce an inferior product.

As stated above, the alloy heretofore con-

sidered best for this purpose is a chromium-aluminum steel. In order to produce a satisfactory case upon chromium-aluminum steels, they are, in practice, subjected to nitrogenation for very long periods of time. As further illustrative of the advantage attendant upon the use of molybdenum, the following examples show the results obtained with such a steel as compared with those obtained with a steel of comparable analysis containing molybdenum, but substantially no chromium. The composition of the steels was as follows, the amounts being given in percentages:

Steel	C	Al	Mo	Cr	Mn	Si	P	S
A-----	0.45	0.93	-----	1.71	0.51	0.26	0.01	0.038
B-----	0.29	0.95	0.92	0.05	0.79	0.15	0.26	0.03

Steel A is typical of that referred to as heretofore considered the best for nitrogenation. Steel B is similar to steel A, but contains molybdenum instead of chromium. Similar samples of each were nitrogenated under similar conditions of ammonia supply, and time, at 540° C. After nitrogenation, the samples were cooled in the furnace and one surface of each sample was ground to a one to twenty taper. Hardness measurements were made on these ground faces, using a Vickers diamond indenter hardness tester. The depth of the case was also measured with a taper gauge. It was found that after nitrogenation for 10 hours, the case formed on steel A was about 0.0055 inch thick, and its hardness expressed in Brinell number, was about 700 at 0.001 inch below the surface. Steel B, after nitrogenation for the same length of time developed a case about 0.01 inch thick, the hardness of which 0.001 inch below the surface was about 825. Samples of each of the above types of steel nitrogenated for 25 hours showed the following results.

Steel	Depth of case in inches	Brinell hardness numbers		
		0.001 inch below surface	0.005 inch below surface	0.01 inch below surface
A-----	0.015	950	730	500
B-----	0.017	975	580	700

In still another test the nitrogenated case formed on a steel containing about 0.75 per cent of aluminum, and about 0.2 per cent of molybdenum was tested for hardness in the manner described above. At 0.001 inch below the surface the Brinell hardness was about 950, and at 0.01 inch it was about 540. As compared with the cases produced when larger amounts of molybdenum are used, this case was not quite as hard toward the surface, but the transition from the case to the core

was more gradual. Such a case is of value for many applications.

The examples just given clearly show one of the differences between the action of molybdenum and that of chromium, in that steel B develops a deeper and harder case than steel A under the same nitrogenation conditions. Another difference between the action of these two metals is shown in the type of case produced, as shown in Figs. 1 and 2 and described in connection therewith.

The examples cited show that nitrogenated cases, equal in hardness and depth to the best previously obtainable, can be produced in materially less time. Likewise, the economy of time results in substantial saving in costs. The coatings produced when molybdenum is used are tougher and more cohesive than those previously known in the art, and they adhere satisfactorily to the unnitrogenated core.

The invention is applicable to various forms of articles which require, or which it is desired to provide with, hard, tough, cohesive and corrosion resistant surface layers. Whatever the article may be, it is first formed, and before being subjected to the nitrogenation process may be heat-treated to give its main body the desired physical characteristics. The character of the case formed by the nitrogenation process may vary depending upon the heat treatment previously given the article. The article is then subjected to any suitable nitrogenation process, as for example by being heated in contact with any substance capable of providing nitrogen in a form capable of causing nitrogenation.

In the examples cited, the articles were nitrogenated at or about 540° C. The heating temperature may, however, vary according to the composition of the article, its shape, etc. It has been stated by Fry that nitrogenation above about 580° C. causes the production of brittle cases, and that nitrogenation must be carried out below this temperature in order to produce satisfactory nitrogenated cases. My experiments, however, have shown that both the rate of ammonia dissociation and of absorption of nitrogen by the article may be at a maximum at higher temperatures, for example at or near 700° C. This is shown in Fig. 3 in which the curves represent data obtained in the nitrogenation of a steel having the following composition:

	Per cent.
Aluminum-----	2.50
Carbon-----	0.19
Manganese-----	0.64
Molybdenum-----	0.83
Phosphorus-----	0.010
Silicon-----	0.29
Sulfur-----	0.023

Curve 1 shows the effect of nitrogenation temperature upon the rate of change of the ammonia concentration in the effluent gas

from the furnace. From 450 to 550° C. the change is gradual, from about 550 to 700° C. the rate of dissociation increases rapidly, and above 700° C. it decreases quickly. Curve 2 represents the effect of temperature upon the gain in weight, plotted as milligrams per square centimeter of exposed surface. This curve follows the same general outline as curve 1, reaching a peak at 700° C.

The curves of Fig. 3 show that with this steel, which falls within the typical analysis referred to hereinabove, the rate of ammonia dissociation and of nitrogen absorption are at a maximum at or about 700° C. The ferrous base articles containing molybdenum according to the invention may be treated at temperatures above 580° C. to produce hard, tough, cohesive, and adherent cases, contrary to the prevailing belief. In many instances it may be desirable to operate at temperatures near the peak of the curve typical of the alloy being treated, because of the increased rate of nitrogenation, and the consequent economies.

Nitrogenated cases are also resistant to corrosion, offering protection against the rusting action of the atmosphere. Ordinary carbon steel appears to become sufficiently corrosion-resistant for most purposes after nitrogenation, but the case is very brittle and spalls or chips off easily. I have found that the tough and coherent nitrogenated case produced on the ferrous base articles according to the invention is satisfactorily resistant to a variety of types of corrosion.

For corrosion resistance, hardness is not usually of prime importance, and I have found that cases possessing satisfactory corrosion resistance and good physical properties may be obtained by nitrogenation at elevated temperatures where the nitrogen absorption is at a maximum, such as at 700° C. Thus nitrogenation for short periods, three hours for example, at 700° C. will give sufficient nitrogen absorption to provide a case which is satisfactorily corrosion-resistant for a wide variety of applications. This decreased time of treatment for such purposes is of course of great commercial importance.

The mechanism of hardening by nitrogenation is obscure, but it is probable that the nitrogen acts by forming a hard nitride or nitrides, and that this or these, being hard, confer that property to the case. The nitrogen hardening may also be due to diffusion of such nitrides to form solid solutions, which are generally of increased hardness, as is well known; and also nitrogen itself may diffuse and form solid solutions. Any, or all, of these phenomena may occur, and others may contribute wholly or in part. Although molybdenum, the use of which characterizes this invention, may increase the hardness by forming solid solutions, its

chief function is to accelerate nitrogen fixation and transference in a manner peculiar to this metal itself. My observations make it seem probable that the mechanism of hardening is about as follows. Iron, when in a massive state, combines with or dissolves nitrogen slowly, so that the hardening process is slow at best, and as previously mentioned, the cases formed on iron or low carbon steel are very brittle. While the physical characteristics of nitrogenated cases are claimed to be improved somewhat by the use of chromium which characterized the alloys previously considered best suited for this purpose, yet even when chromium is used the nitrogenation period has been long, because the chromium nitrogenation products form slowly and are relatively stable. The stability of such products materially delays the progress of nitrogenation, because they do not readily give up nitrogen to the metal, or otherwise assist in hastening the hardening action.

Molybdenum, however, appears to readily take up nitrogen in the form liberated in the dissociation of ammonia, and furthermore, the nitrogen thus taken up is apparently readily liberated in a form in which it diffuses most readily through the solid metallic matrix. Some of the nitrogen thus taken up is set free, and diffuses inwardly into the surrounding metal to form solid solutions and nitrides. It appears also that when the concentration has become sufficient, a compound analogous in character and hardening action to iron carbide is deposited. This compound may, for lack of a better term be called nitride-cementite, because of its appearance under the microscope. At the same time the molybdenum below the surface has been receiving nitrogen by this diffusion from that nearer the surface, and it in turn liberates nitrogen for rediffusion. Thus beginning at the surface, and passing progressively inward, the molybdenum takes up nitrogen and liberates it, and by virtue of this action the nitrogenation is much more rapid than was heretofore known where the sluggish direct diffusion of nitrogen itself was probably the chief or only factor. In addition the faster or more ready diffusion of the nitrogen or nitrides caused by molybdenum, produces superior results

because more uniform distribution is secured.

From the foregoing it sufficiently appears that according to this invention there are provided at reduced cost of manufacture ferrous base articles which have improved surface layers produced by nitrogenation. As has been explained, these advantages are attained by the addition of molybdenum to iron combined with carbon, and particularly by the addition of molybdenum to steel which preferably also contains aluminum.

No claim is made herein for the method of forming a nitrogenated case on the surface of a ferrous base alloy, the method herein disclosed being claimed in a divisional application.

According to the provisions of the patent statutes, I have explained the principle of my invention, and have specifically described what I now consider to represent its best embodiments and the manner in which its advantages may be attained. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described. Furthermore, I desire to have it understood that the foregoing explanations of the action of molybdenum in the progress of nitrogenation are not limiting. While I believe the action to be as explained, it may nevertheless be otherwise.

I claim as my invention:

1. A ferrous base article of manufacture containing molybdenum as a characterizing element, and having a hard, tough, coherent and adherent nitrogenated surface.
2. A ferrous base article of manufacture containing from a substantial amount up to about 4 per cent of molybdenum as a characterizing element, and having a hard, tough, coherent, and adherent nitrogenated surface.
3. An article of manufacture composed of a steel containing from a substantial amount up to about 4.0 per cent of molybdenum as a characterizing element, and about 0.1 to 4 per cent of aluminum, and having a hard, tough, coherent and adherent nitrogenated surface which is resistant to atmospheric corrosion.

In testimony whereof, I sign my name.

WILLIAM H. PHILLIPS.