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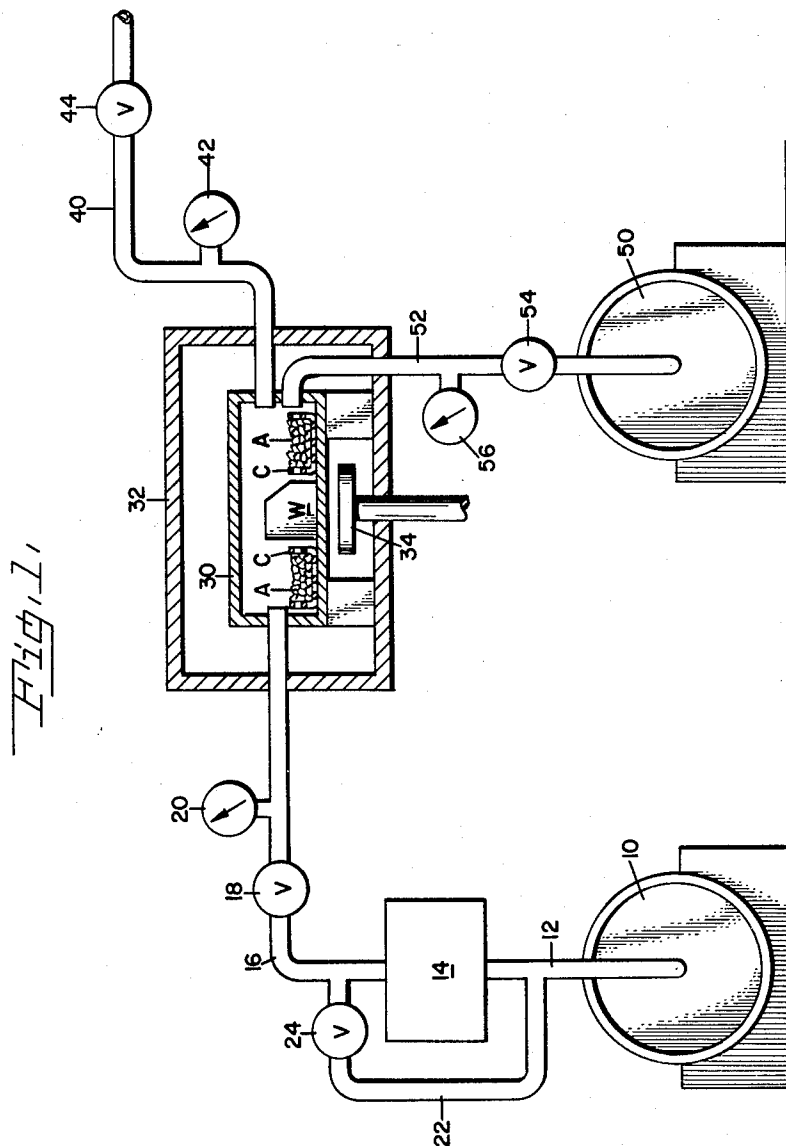
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3,140,205

PROCESS FOR NITRIDING STEELS OF THE LOW, MEDIUM AND HIGH
ALLOY TYPES BY FIRST REMOVING THE PASSIVE
OXIDE SURFACE FILM

Filed July 26, 1962

2 Sheets-Sheet 1



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TEMPERATURE

TIME

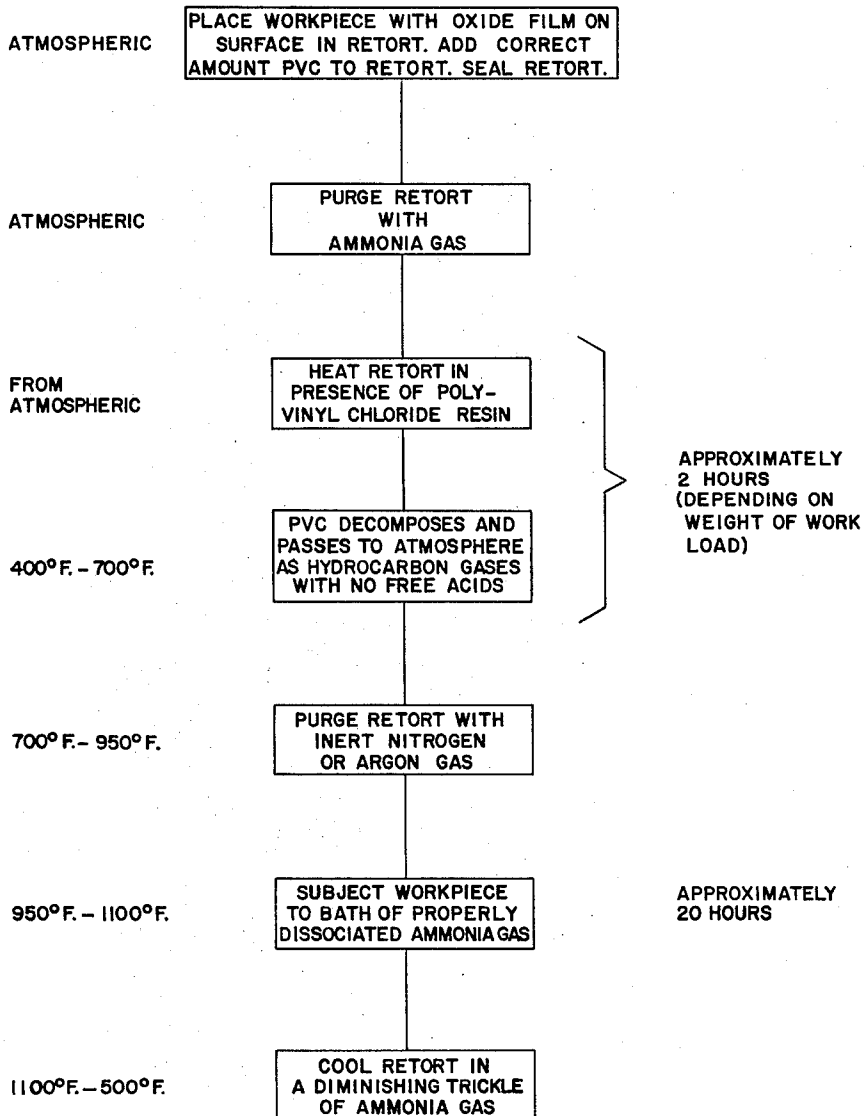


Fig. 2

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PROCESS FOR NITRIDING STEELS OF THE LOW, MEDIUM AND HIGH ALLOY TYPES BY FIRST REMOVING THE PASSIVE OXIDE SURFACE FILM

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This invention comprises improvements in a process for producing super-hard surfaces of steels of the low, medium and high alloy types, where it is desired to provide a hard case and a relatively soft, ductile core, which as a procedure is characterized by directness, simplicity, and speed leading to improved metal surfaces which will better resist the destructive effects of seizure, abrasion, fretting, brinelling, temperature, and plastic deformation and corrosion of parts in areas of intimate contact under heavy pressures and relative motions.

It has long been apparent that the resistant, inert or passive, oxide film on the surfaces of metallic work pieces must be completely removed before any nitriding procedure ensues, if optimum results in the case hardening in a nitrogenous atmosphere are to be obtained, it being known that said film increases the resistance of nitriding. Without such treatment, there is a consistent obtainment of a surface which lacks uniformity of case structure and its hardness and wear-resistance is greatly reduced, due to an inefficient or improper initial removal of such oxide film and/or to a reformation of the oxide (reoxidation) subsequent to the cleaning operation and prior to the nitriding treatment. Sometimes no case is formed within any reasonable treatment time; sometimes the case which is formed is too shallow or of too low a degree of hardness.

In the nitriding process, the presence of said oxide film, commonly referred to as the passive film, serves to prevent or to substantially restrict the penetration of the nitrogen and its absorption by the surfaces of the metallic work pieces.

Such difficulties are overcome, according to the present invention, by treating the surfaces of the metallic work pieces to the action of reducing gases and followed immediately, before the surfaces so treated can come under any oxidizing influence, and while they are still under the influence of the passifying agent, by the nitriding process.

The present invention consists in the several operational steps and in the relation of each of the same to one or more of the others, said operational steps being sequential and uninterrupted and comprising, all within a single sealed-from-atmosphere situs: preliminarily, creating an oxygen-free atmosphere within the situs; secondarily, pretreating the surface of the work piece to be hardened by effectuating removal of the passive oxide film through the reacting of the circulating gaseous derivatives of a catalytic agent at the gas-solid interface; thirdly, purging the situs of the gaseous products of the catalytic agent; and lastly, subjecting the work piece to a circulating nitriding gas such as nitrogen liberated by the decomposition of ammonia, which nitrogen is absorbed by and forms nitrides with the iron and special alloying elements present in the steel, the nitrides being precipitated at the nitriding temperature.

The sequential steps, when followed uninterruptedly in seriatim, will be comprehended as offering the singular advantages in a method of removing the oxide film from the metal and of nitriding as a part of the same procedure where the entire procedure consumes a time period which is of markedly less duration than the time period

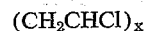
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heretofore required for the nitriding step alone, thus effectuating appreciable savings in the ammonia consumed in nitriding and materially reducing furnace time. For example, the time cycle in the area of 100 hours necessitated in prior art nitriding processes is herein reduced to a time cycle more closely approximately a time period in the area of 20 hours, with the concomitant advantage that a nitride case of markedly increased depth is obtainable as compared with the results previously obtained.

It is recognized that a mere nitriding treatment involving the blanketing of a work piece within an atmosphere of a nitrogen-liberating gas in and by itself, fails effectively to serve in activating or catalyzing the work piece surface and in ensuring the desirable formation of a uniformly-hard nitrided case.

I have determined that polyvinyl chloride resin offers a capacity for decomposing, under proper conditions of temperature, so as to generate pyrolysis products capable of activating the work piece surfaces preparatory to nitrogenization by the removal of the oxide film therefrom and that my purposes are attainable in the way of providing an improved nitride case in a far shorter time period, and all in a conventional nitriding furnace and within the conventional range of nitriding temperatures, provided the preparation for the nitriding is carried out in the presence of such gaseous products of a proper proportion of polyvinyl chloride resin, introduced into the retort and subjected to heat of a predetermined temperature.

Said activating agent, sometimes identified as PVC, and having a formula:



is a fine, granular, nontoxic, tasteless, odorless, nonflammable resin properly processed so as to decompose thoroughly in a desired temperature range and time period and exhibiting a superior capacity for being milled or extruded or otherwise molded into pelletized form.

The PVC, when properly processed, will be in the form of hard pressed pellets so that water cannot penetrate thereto, thus precluding liquescence.

PVC which has been improperly processed or when used in too large quantities for the work pieces being treated, will not thoroughly decompose, thus leaving an objectionable soot-like layer on the work pieces precluding fully effective nitriding.

Said activating agent, when used in the proper amount, lends itself admirably to the process hereof inasmuch as it exhibits a complete decomposing capability offering vapors having a reaction within a range of temperatures below the nitriding temperature range, wherefor the process may be carried out during a time interval while the temperature within the atmosphere-free enclosure is on the ascendancy to the said nitriding temperature level and whereby, the generated gaseous derivatives function to activate the work piece surfaces immediately prior to their evacuation therefrom and the introduction of the dissociated ammonia sufficient to make available an abundance of nascent nitrogen where the surface hardness is imparted to the material by the absorption of the nitrogen.

The activating action offers an improved superactive surface such as to allow an accelerated nitriding rate when and as such succeeding step in the sequential series of operations ensues uninterruptedly therefollowing.

It will be understood, ab initio, that the nitride hardening steps is carried out, not in the presence of the activating or reducing agent and/or its gaseous products, same having been exhausted from within the sealed area immediately prior to the introduction thereto of the nitriding agent, and also that, obligatorily, the reducing agent, having the capacity for generating the gaseous activating prod-

ucts envisioned herein, shall not come into physical contact with the work piece within the sealed area, any sprinkling of the reducing agent upon any surface or any like system being specifically to be guarded against.

In the annexed drawings, I have shown, in FIG. 1, a diagrammatic elevational view, with certain parts in section, of a typical apparatus for carrying out the method of the invention, and, in FIG. 2, a flow chart showing the series of sequential steps in said method.

A supply source 10 of ammonia, such as commercial anhydrous ammonia, is connected, by a conduit 12, to a conventional cracking unit 14 serving to dissociate the hydrogen and nascent nitrogen constituents of said ammonia led therefrom under a predetermined positive pressure along a conduit 16 having conventional pressure regulating and indicating means 18 and 20 respectively provided therealong.

A by-pass conduit 22, having suitable valve means 24 provided therealong, may be so disposed as to by-pass cracking unit 14.

Conduit 16 leads directly to a sealable nitriding retort 30 disposed within a suitable metallurgical furnace 32 fired by electric, gas or oil means 34 of conventional design.

An exhaust conduit 40 serves to conduct waste products of the sequential purging, reducing, purging and nitriding actions to the atmosphere and is provided with conventional indicating means 42 and pressure regulating means 44 therealong.

Retort 30 is of a configuration adapted to receive one or more work pieces W and a supply of the activator A, said activator preferably being placed in the lower regions of the retort and within one or more apertured containers C to preclude physical contact of any portion thereof with the work piece.

Upon sealing retort 30, after the work pieces W and the activator A have been placed therein, it is purged of oxygen by the flowing therein of a quantity of pressurized raw ammonia gas, at atmospheric temperature, and led from source 10 through conduit 12, by-pass 22, and conduit 16 to the retort interior, the purged air being exhausted through conduit 40 under the force of the raw ammonia gas therebehind. Following such purging, the flow of the raw ammonia gas is terminated by the appropriate valve means and heating element 34 is then energized for effectuating the raising of the temperature in retort 30 from atmospheric temperature to a temperature in the vicinity of 700° F. during a time interval (at least of 2 hours duration) sufficient to assure that the work piece attains the desired temperature.

It will, of course, be understood that the time involved will be directly related to the size and/or number of work pieces involved.

As this heating procedure ensues, activator A decomposes, slowly commencing so to decompose at approximately 300° C. and increasing in rate of decomposition in direct ratio to the temperature increase, being completely decomposed at approximately 700° F.

Retort 30, being sealed, accordingly fills with the gaseous decomposition products of activator A, wherefor the generated gas circulates around and blankets work piece W in manner to activate the surfaces thereof, thus effectively removing the passive oxide film therefrom.

When the retort temperature reaches 700° F., an inert nitrogen or argon gas from a source of supply 50 is introduced to the retort through a conduit 52, having conventional pressure regulator and indicating means 54 and 56 respectively provided therealong and is allowed to flow therein until the retort temperature rises to 950° F., during which period, it serves to sweep out from within the retort the products of the decomposition of the reducing agent through conduit 40 to the atmosphere as hydrocarbon gases with no free acids,

The flow of nitrogen or argon gas is shut off, and the retort temperature is raised to 1100° F., wherefor a timing of approximately 20 hours at said 1100° F. temperature, may be initiated, by the introduction of a flow of ammonia from source 10 through conduit 12 to cracking unit 14 for dissociation into nascent nitrogen and ammonia which flows along conduit 16 to retort 30.

During the first two or three hours of the 20 hours cycle, a dissociation of 20% is preferentially, though not obligatorily, maintained.

During the remaining hours of the 20 hours cycle, the dissociation rate is increased to 40%, although conceivably it may go to 60-80%.

At the termination of the 20 hours cycle, the furnace is shut off and the flow of nitrogenizing gases is gradually diminished to a trickle while the retort temperature is allowed to reduce to 500° F., at which point the flow is completely shut off.

For the production of a minimum of the so-called "white layer," it may be desirable to reintroduce inert nitrogen or argon gas from source 40 along with the dissociated gases so that a high dissociation rate is maintained, especially toward the end of the 20 hours cycle.

The amount or weight of activator necessary properly to activate the work piece surfaces preferentially bears a relationship to the total surface area of the work. Because of the varying sizes and shapes of the work and further because of the fact that the work is normally processed in mixed loads, I have arrived at an approximate ratio of weight of work versus weight of activator: for the stainless steels, this ratio is about 20 grams of activator to 100 pounds of work; when nitriding the low alloy steels, the ratio is about ½ gram of activator to 100 pounds of work; it thus being obvious that approximately 40 times as much activator is used for the stainless steels as is used for the low alloy steels, due in main to the resistance of the stainless steels to the action of the activator.

What it is desired to claim and secure by Letters Patent of the United States is:

1. The improvement in the hardening of the surface of a metallic work piece characterized by the presence on the surface thereof of a passive film acting to inhibit penetration of nitrogen into the surface when such work piece is heated in a nitrogenous atmosphere comprising, heating the work piece at a temperature between 400° and 700° F. during a time interval of at least 2 hours duration in the presence of the gaseous products of a decomposed polyvinyl chloride resin and subsequently at a temperature of 1000° F. during a time interval of approximately 20 hours duration in the presence of a nitrogen-liberating gas.

2. The improvement in the hardening of a metallic article characterized by the presence on the surface thereof of a passive oxide film serving to inhibit penetration of nitrogen into the surface when such article is heated in a nitrogenous atmosphere comprising the steps, heating the article directly with a preliminary depassifying treatment at a temperature between 400° F. and 700° F. for a minimum of 2 hours in the presence of the gas of decomposed polyvinyl chloride and continuing the heating treatment in the presence of a nitrogen-liberating gas for approximately 20 hours.

References Cited in the file of this patent

UNITED STATES PATENTS

1,958,575	Hengstenberg	May 15, 1934
2,057,813	Babinet	Oct. 20, 1936
2,789,930	Engelhard	Apr. 23, 1957
2,851,387	Low	Sept. 9, 1958