Sept. 21, 1943. J. W. HARSCH 2,329,896

METHOD OF AND COMPOUND FOR CARBURIZING

Filed Jan. 28, 1941 2 Sheets-Sheet 1

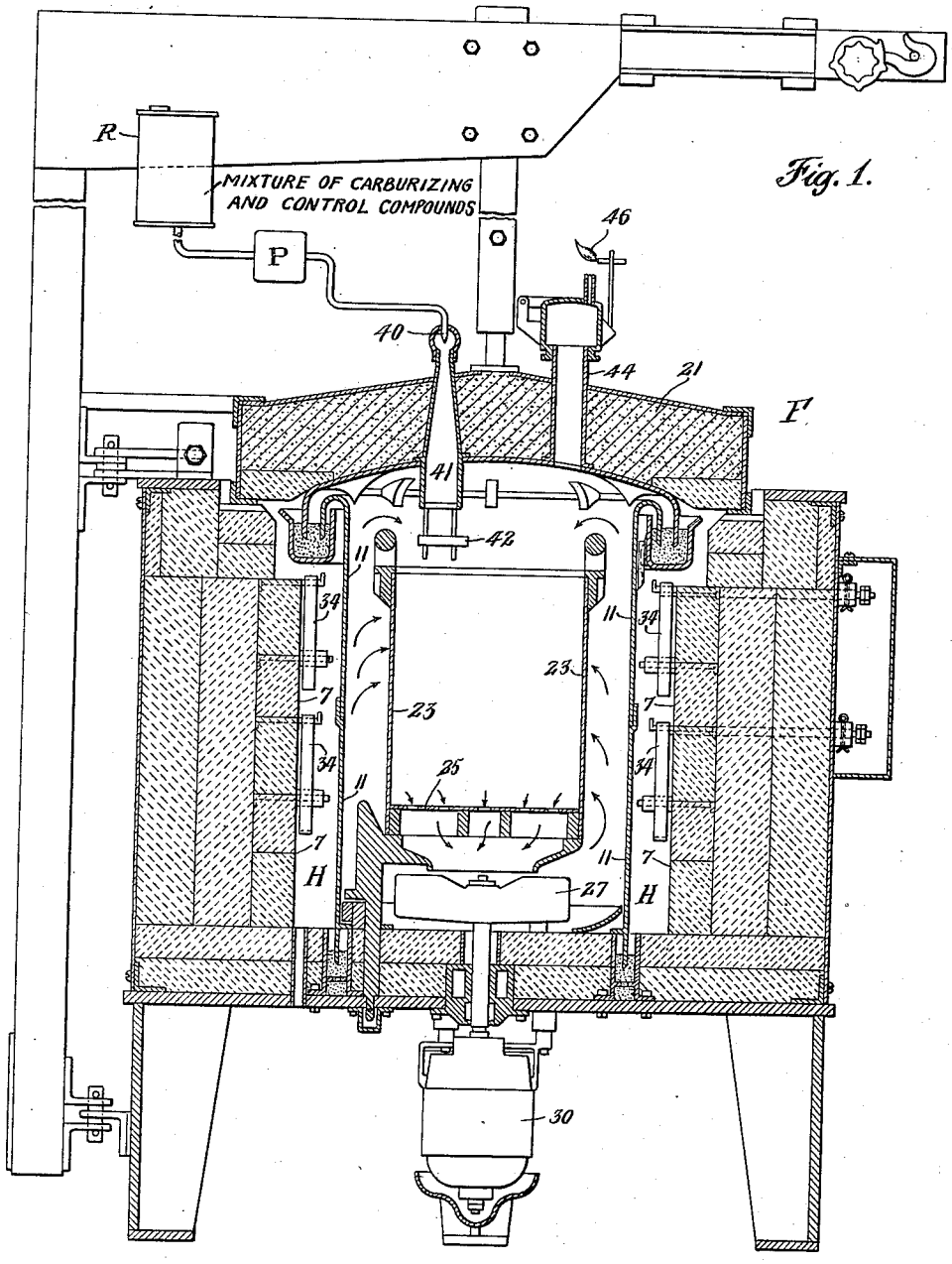


Fig. 1.

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Fig. 3.

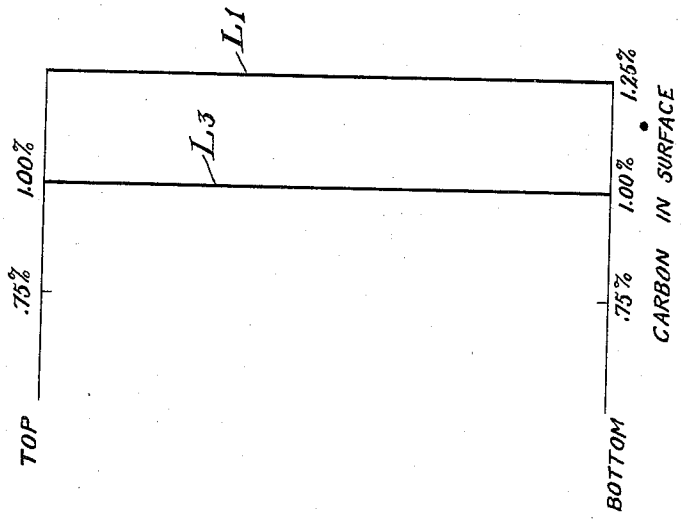
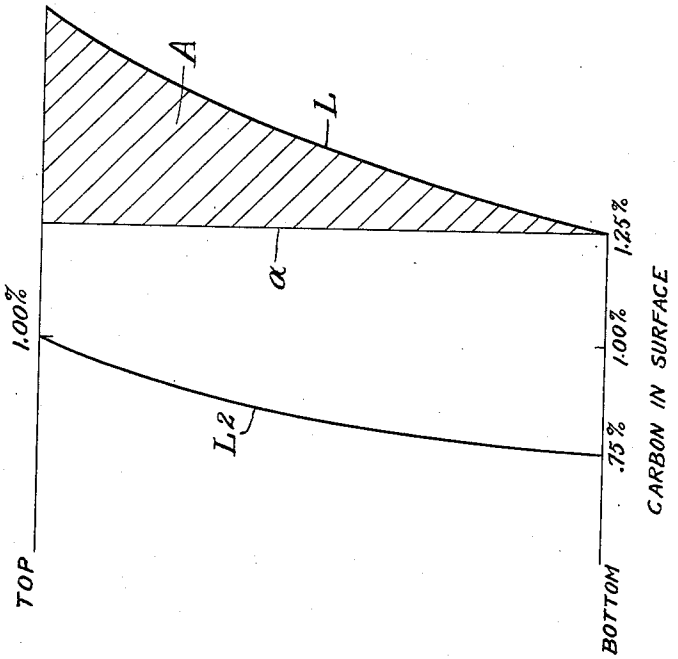


Fig. 2.



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UNITED STATES PATENT OFFICE

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METHOD OF AND COMPOUND FOR CARBURIZING

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Application January 28, 1941, Serial No. 376,270

12 Claims. (Cl. 148—17)

My invention relates to methods of and compositions utilizable for carburizing or producing diffusion alloy cases upon steels, alloy steels and the like, herein generically referred to as steel or as the load or work, by subjecting them at carburizing temperatures to nascent or atomic carbon yielded upon application of heat to or cracking of suitable carbonaceous compounds, in association with compounds which beneficially influence, control, the processes of carburization.

One of the principal objects of my invention is the elimination or marked reduction in the amount of soot formed, or in its rate of production, when the amount or rate of carburization is such as to effect surface saturation, i. e., saturation of the surface of the work with carbon.

Another of the principal objects of my invention is to procure uniformity or enhanced uniformity of surface subsaturation, i. e., concentration of carbon in the surface of the work at a degree below saturation, from one limit to another of the load.

A distinct further object of my invention is improvement of the methods described in my prior U. S. Patents Nos. 2,161,162 and 1,999,757; and Eberle et al. Patent No. 2,056,175; and improvement of gas carburizing methods in general.

In so-called gas carburization herein contemplated, the case-forming carbon, which combines with the steel to form a steel-carbon diffusion alloy case, is, as in carburizing methods heretofore known, yielded by a carburizing compound (herein consisting of a suitable carbonaceous material or a mixture of carbonaceous materials) upon heating thereof to suitably high temperature, such as the carburizing temperature of the steel itself or some other higher or lower temperature existing at a point or region in the carburizing system more or less remote from the load itself; that compound may be such that aforesaid heating thereof effects cracking or dissociation thereof.

In accordance with my invention, in carburizing to effect on the steel a case characterized by either surface saturation or surface sub-saturation, there is associated in mixture with aforesaid carburizing compound a control compound, consisting of a single compound or a mixture of compounds, in suitable respects differing in character from the carburizing compound; and, preferably at least throughout passage of the associated control and carburizing compounds in intimate mixture through the load or work, they are subject to substantially the same immediate external or ambient thermal conditions, whereby such use of the control compound under those thermal conditions so changes the character and the results of the carburizing process that there are attained aforesaid objects of my invention and the hereinafter expressed further objects and advantages, and those inherent in the described methods involving the use of aforesaid control compound.

When the carburizing compound or a component thereof is cracked, at or about carburizing temperature, usually within the range from about 1500° F. to about 1800° F., generally about 1700° F., to yield case-forming carbon, the control compound influences, thermally controls, the rate or amount per unit of time, of aforesaid cracking of aforesaid carburizing compound or component thereof. The thermal control, of broad application in gas carburizing, is effected by governing to suitable extent and at suitable rate the amount of or rate of application of heat available for cracking aforesaid carburizing compound or component thereof by utilizing a suitable proportion of the heat, dependent upon the nature of the control compound and its proportion in the mixture thereof with the carburizing compound, otherwise available at or immediately adjacent any given portion of the carburizing compound for cracking it, in endothermically cracking the immediately associated or adjacent portion of the control compound, carbonaceous or not, differing in character from said carbonaceous material in that it yields on cracking thereof no case-forming carbon or significantly, very much, less case-forming carbon than required by that portion of the work affectable by said portion of the carburizing compound. More particularly, as in the instances herein more in detail described, when the vehicle gas, the carburizing compound and the thermal control compound progress through or along the work from entry into to exit of gases from it, the load, the thermal control slows the progress of cracking of the carburizing compound, with marked improvement in or attainment of substantial uniformity, from one end to the other of the work charge or load zone, of the amount of or rate of cracking of the carburizing compound, with resultant saving of carburizing material and attainment of aforesaid objects and other advantages.

Another aspect of my invention resides in suitably correlating, matching or adapting the inherently generally very rapid or very high rate of cracking, at or adjacent carburizing temperatures, of the carburizing compound with or to

the velocity of travel, through the work or from entry into to exit from the load or load zone, of the vehicle gas, which carries or with which is mixed the carburizing compound and/or the products of cracking thereof, with the effect of causing a given amount of the carburizing compound to travel farther, in its passage through or with respect to the load, during the period of cracking thereof.

My invention resides in the hereinafter described methods, and the compositions utilizable in practicing them.

For an understanding of my invention, reference is had to the accompanying drawings, in which:

Fig. 1, partly in section and partly in elevation, is illustrative of one of the many forms of apparatus utilizable for practicing my methods;

Figs. 2 and 3 are graphs explanatory of principles relating to my invention.

Referring to Fig. 1, F is a furnace structure illustrative of one of many forms of circulatory carburization furnaces; in any event it serves for explanation of the underlying principles of my invention, whether or not forced circulation be employed.

The furnace of Fig. 1 hereof is similar to that illustrated in Fig. 1 of my prior United States Patent No. 2,168,028, utilizable for methods of carburizing which, among many others now known, are capable of improvement in accordance with my present invention.

In Fig. 1, R is a container or reservoir in which is stored a mixture in suitable proportions of at least those of the mutually suitable of the hereinafter described carburizing and control compounds, which mixture usually is liquid at ordinary temperatures and pressure. By the positive displacement pump, indicated at P, the mixture in reservoir R is delivered, through the piping indicated, at definite or metered rate suited to the requirements and dependent upon speed or other operating characteristic of the pump, to the nozzle **40** from which it drops through tubular member **41** on to the vaporizing plate **42** disposed close to the upper end of the container or basket **23** in which is disposed the work or load, in the form of one or many pieces of steel or alloy steel. The load zone is approximately the space or volume occupied by the load held by the basket. The load is brought up to carburizing temperature by circulating the furnace gas downwardly through the basket in contact with the work or load therein, through the circulating fan **27**, which may be of blower type, driven by electric motor **39**, thence upwardly to the upper end of the basket in the space between the exterior of the basket **23** and the retort wall **11** to which is transferred heat from the sources of heat shown, for example, as electric resistors **34**, disposed in the chamber H.

When the work in basket **23** has attained carburizing temperature, feed of mixture of carburizing and control compounds from reservoir R is established, and continued at desired or suitable rate, either constant throughout the carburizing run, or varied either in steps or gradually to increased or decreased magnitudes, as may be desirable.

The mixture passes in contact with the load, through it when comprising pieces, from one limit to another thereof, which limits in the example illustrated are the top and bottom of the load.

Upon impingement of aforesaid mixture upon the plate **42**, it is vaporized, and the vapors of the carburizing and thermal control compounds are carried by the vehicle or furnace gas downwardly through the load in contact with the surfaces thereof throughout. The carburizing compound or a component thereof is or may be cracked at or adjacent the surface of the work piece or pieces, yielding nascent or atomic carbon which reacts with the steel at the surface thereof by way of formation of a carburized case or diffusion alloy. The control compound or a component thereof of aforesaid mixture also is or may be concurrently cracked, and in cracking absorbs a portion of the heat available from or imparted by the work or vehicle gas so reducing the amount of heat available for cracking the carburizing component or components of aforesaid mixture, and so thermally controlling, generally by restraint thereof, the rate of production of case-forming carbon and the rate of addition of carbon to the work at its surface.

In general, the thermal control so effected slows the progress of cracking of the carburizing compound or a component thereof, so spreading out or rendering more uniform, from top to bottom of the basket **23**, or from top to bottom of the load therein, the rate of cracking of the carburizing compound of aforesaid mixture, nevertheless leaving at the bottom of the load or basket enough of the carburizing compound there to be cracked to effect or maintain the desired degree of concentration of carbon in the work at its surface.

A carburizing compound which cracks at carburizing temperatures does so very quickly or at very high rate, and, in consequence, the distance through the load traveled during cracking of an incremental portion of the carburizing compound is extremely short; this means, especially in the case where the carburizing compound is rich in carbon, as in the case of long-chain carbon compounds, cracking at high velocity, very quickly or at high intensity or rate, during travel over only a short distance through the load, produces, at great rate at or near entry into the load zone or work and diminishing as the exit is approached, carbon atoms or case-forming carbon considerably more rapidly than the steel or work requires for or at its maximum rate of absorption of carbon. The result is that even though, as described in my Patent No. 2,161,162, the carbonaceous material, which furnishes the case-forming carbon, is introduced into the vehicle gas in advance of and adjacent its first contact with the work or load, nevertheless the quickness or velocity with or at which the cracking takes place is such that when sufficient of the carbonaceous material is introduced to last to the extent required by the work all the way through the load or charge, excess carbon beyond that absorbed or absorbable by the steel becomes available, resulting in formation of more than the desirable or allowable amount of soot. Otherwise stated, the slope, "die-out" or rate of decadence of the cracking reaction of the carbonaceous material furnishing the case-forming carbon is so rapid that when sufficient of it is introduced to prolong the cracking reaction, as it must be, throughout to the exit of gases from the work or load, the region of entry into the load and beyond is over-supplied with carbon resulting from the too rapid cracking reaction.

By my thermal control, however, the velocity or quickness of the cracking reaction or other effect of heat application of or to the carbona-

ceous material which furnishes the case-forming carbon is restrained, slowed or reduced in amount or rate, to spread out the cracking reaction or the formation of case-forming carbon over greater extents of space in the load zone, so to adapt the amount and rate of production of case-forming carbon to a magnitude not undesirably in excess of the carbon requirement of the work, and to cause the cracking reaction suitably to take place essentially at one and the same or a uniform rate, as the cracking for production of case-forming carbon progresses through the work or work-chamber.

My thermal control changes the tendency, which is toward high intensity of cracking or production of case-forming carbon at the region of introduction into the load of the carbonaceous material which furnishes that carbon and toward relatively low or lower intensity at the exit of gases from the charge or load, to an action which may be characterized as rendering more nearly uniform or substantially uniform, from top to bottom of the load, the intensity of cracking of that material, so rendering more uniform the concentration of carbon in the case from end to end of the load, whether that concentration be such as either to effect saturation of the surface of the work with carbon or to effect sub-saturation at the surface of the work.

With the improvements procured by my control compound, whatever be its specific behavior or nature of its action so long as it have the general effects herein described and inherent from its association with the carburizing compound, there is cumulatively effective such increase in uniformity of carburization or case formation as may be contributed by circulation of gases in or through the furnace or carburizing chamber. In any event, even in the absence of such circulation my control compound nevertheless effects substantial or marked improvement in uniformity of surface concentration of carbon from entrance to exit end of the load, avoids production of soot, and effects economy of carburizing material and other advantages.

While in discussion of Fig. 1 the carburizing and control compounds were considered as bearing a fixed ratio to each other, by volume, it shall be understood that the proportions of the carburizing and control compounds may be varied by feeding each at a variable but metered rate into the carburizing system or furnace, yet maintaining constant the rate of feed of the total of the two compounds, or varying the rate of feed of that total whatever may be the determined proportions of the two compounds to each other.

When the carburizing and control compounds are solids, or either of them is a solid, they or it may be dissolved in a suitable compound, still maintaining desired proportions of the carburizing and control compounds themselves while maintaining the proper rate or rates of feed of the two compounds combined, or individually if separately fed; the solvent or solvents for the solid or solids may themselves be carburizing and control compounds or a carburizing compound or a control compound; or the solvent or solvents may be neutral in the sense of operating as neither a carburizing nor a control compound.

It shall be further understood that the carburizing compound and/or control compound may be, besides liquid or solid, a vapor or vapors, or gas or gases.

A desideratum is that the carburizing and control compounds be in intimate mixture in passing through the load, or before or when entering the vehicle gas of the carburizing system; that they may be introduced in intimate mixture or separately, and become intimately mixed within the carburizing system and be so especially throughout the load; and may be introduced at the same time or at different points either adjacent first contact with the load or at some remote point or points.

Notwithstanding circulation, effected by fan or otherwise, in the past has been contributing to uniformity of carburization effected, nevertheless there has heretofore always remained or existed non-uniformity of availability of carbon in the sense that there has been decadence or "die-out" of production of carbon, whether or not all the carbon produced actually combined with the work in forming a case thereon, from entrance of the carburizing agent into the load, as at the top of the load in the basket 23, Fig. 1, to the exit or bottom of the load, as at the bottom of the basket, for the conditions of both surface saturation and surface sub-saturation.

In Fig. 2, where surface saturation, e. g., 1.25% carbon is obtained from top to bottom of the load, aforesaid "die-out" or decadence in production or yield or carbon is, for illustrative purposes, represented by a hypothetical characteristic L whose assumed slope or inclination, with respect to the vertical ordinate or the line "*a*" of a length corresponding with the vertical depth of the basket or load, represents aforesaid decadence of production of, as distinguished from carburization or case formation by, the carbon derived by application of heat to the carburizing agent at carburizing temperature. That is to say, the ordinate *a* of Fig. 2 corresponds with surface saturation of the work, to wit, 1.25% carbon in the surface of the steel (such, for example, as a straight (non-alloy) steel of .2% carbon before carburization). The rate of feed or input of carburizing agent in Fig. 2 is assumed to be just sufficient to last throughout the load to the bottom thereof and there still to produce aforesaid surface saturation.

The shaded area A of Fig. 2 represents that amount of carbon produced from the carburizing agent which the work has not been capable of utilizing in case formation, and which has become the undesired by-product, soot. The greater the area A or the amount of soot or unused carbon produced, the greater the waste of carburizing agent and the greater the inefficiency of the method from that standpoint.

Fig. 2 more particularly connotes the situation where the carburizing agent is introduced into the vehicle gas in advance of but adjacent its point or region of first contact with the work, as at the top thereof, Fig. 1; this is the situation particularly dealt with by my aforesaid Patent No. 2,161,162. However, what is here said respecting Fig. 2, is also applicable to the case where the carburizing material is delivered into the furnace gas at a point or region remote from its first contact with the load, in which case even more carburizing agent is required to be supplied, and much more is wasted as soot than represented by aforesaid area A.

The non-uniformity of production or availability of carbon from the carburizing agent from entry into to exit from, or from top to bottom of, the load, as indicated in Fig. 2, is, in accordance with my invention, at least markedly diminished, and may be substantially eliminated by recourse to my control compound, of suitable

composition and proportion with respect to the composition and amount of the associated carburizing compound, and by feeding the mixture of those compounds to the load at a rate suited to the length of the path through the load traversed by the mixture from top to bottom of the load.

My control compound has the effect of reducing the slope of characteristic or line L, Fig. 2, and of rendering it of zero slope, or vertical, as indicated by hypothetical characteristic L1, Fig. 3, the import of which is that surface saturation still obtains from top to bottom of the load, with production of no soot or unused carbon, with no waste of carburizing compound, connoting increased efficiency in that respect, more than justifying the cost and use of the control compound.

The same principle applies in cases where a predetermined surface sub-saturation is required, in which instances no soot is formed, because all of the carbon available and produced from the carburizing compound is consumed in case formation.

Returning to Fig. 2, hypothetical characteristic L2 has a slope representing an assumed decadence in availability or production of carbon, from the carburizing compound, all of which is usefully absorbed by the work but yielding a non-uniform sub-saturation of carbon in the surface of the work varying from an assumed required sub-saturation of say 1.00% at the top of the work to a too low sub-saturation of say .75% at the bottom of the load. This lack of uniformity is corrected by application of my principle of use of the control compound, by which the slope of characteristic L2, Fig. 2, becomes zero, then appearing as the vertical characteristic L3, Fig. 3, connoting uniform sub-saturation from top to bottom of the load.

In practice, this uniformity of carburization from end to end of the load at predetermined sub-saturations is much sought after.

In the case of the hypothetical characteristic L2, Fig. 2, for sub-saturations in percents concentration of carbon at the work surface throughout the depth of load, the sub-saturation magnitudes are measures of the concentrations, at the corresponding depths in the load, of the case-forming carbon available at those depths; the characteristic therefore indicates the departure from uniformity of available carbon from the amount thereof essential for uniformity of sub-saturation from top to bottom of the load, whereby it is then possible to determine in any case what change in carburizating and/or control compounds may be in order, their relative proportions whether or not either or both compounds be changed, and the rate of feed of their combination to procure the desired sub-saturation, uniform from top to bottom of the load.

And when a combination of any particular carburizing and control compounds, for given proportions thereof, procures practical uniformity from top to bottom of the load of carbon production and case formation at one magnitude of sub-saturation, any other magnitude of surface sub-saturation, within wide practical limits, may be obtained by changing the rate of feed of the combined compounds, without changing their proportions; and the rate of feed may be raised to such magnitude as to be just sufficient at the bottom of the load there to produce surface saturation, in which event the concentration of carbon in the surface of the load from top to bottom is uniform, and no soot is formed.

The compounds utilizable as the carburizing compound or as components thereof are extremely numerous; they are exemplified by such materials as, when heated to carburizing temperatures, yield case-forming carbon in suitable amounts.

Preferably they are such compounds as are characterized by mutually bonded carbon atoms of hydrocarbon compounds or of compounds of carbon, hydrogen and oxygen; some have carbon atoms doubly and triply mutually bonded, the latter having or yielding the higher carburizing potentials.

Among aforesaid compounds are ethane, ethyl alcohol, propane, propyl alcohol, butane, butyl alcohol, butaldehyde, pentane, amyl alcohol, amyl aldehyde, valeric acid; hexane, heptane, octane (and the further hydrocarbons of the same series, richer in carbon) and their corresponding mono-hydric alcohols, aldehydes, their mono-basic acids; and the various isomers of all aforesaid compounds; mineral oil waxes and greases, including paraffin waxes, fatty acids such as stearic acid and the like. There are also included carbonaceous compounds of hydro-cyclic and hydro-aromatic types, such as cyclo-hexane, turpenes, limonenes, including dipentene; turpentine, benzene, the aromatic hydro-carbons; and hydro-carbons of the acetylene series.

Compounds utilizable as or as components of the control compound comprise:

Those carbonaceous compounds, represented by the lighter alcohols of the mono-hydric type, including methyl and ethyl alcohols; dihydric alcohols, and polyhydric alcohols including glycerine; aldehydes and ketones; and dibasic and polybasic acids; and isomers of aforesaid compounds. Amines also may be used.

In general, as the number of carbon atoms of these carbonaceous compounds increase, then their corresponding dihydric alcohols or polyhydric alcohols would be used, or the dibasic or polybasic acids would be used. That is to say, it is in general preferred that control compounds be used in which there shall be no more than two carbon atoms which are not respectively mutually bonded to like number of oxygen atoms; they may contain any number of carbon atoms so long as they are mutually respectively bonded to like number of oxygen atoms, provided the total number of oxygen atoms shall not exceed the number of carbon atoms.

It is to be understood the above classifications of carburizing and control compounds are not in all cases distinct from each other, for in some cases a compound above classified as a control compound may be utilizable as a carburizing compound, or a compound above classified as a carburizing compound may be used as a control compound, depending upon the carburizing temperature and the surface concentration of carbon desired; none of such compounds is utilizable alone concurrently to serve both as the carburizing compound and at the same time as the control compound for modification or control of its own rate of yield of carbon in its passage through the load.

In general, the carbonaceous control compounds are those, whatever their types, classes or other characteristics, which on application thereto of high, particularly carburizing, temperatures or which crack at those temperatures, do not yield amounts of case-forming carbon at all significant per se, or at most are insignificant with respect to the amounts of case-forming

carbon produced by the associated carburizing compound.

In view of practical considerations, including availability of the compounds on the market, their cost, and suitability, there follow several examples of their use, all dealing with carburization of straight carbon (non-alloy) steel of .2% carbon, in pieces constituting a load of 400 pounds, of about 18 inches depth from top to bottom in a cylindrical basket about 15 inches in diameter, in a furnace such as illustrated in Fig. 1, with a circulating fan speed of 1725 revolutions per minute, runs of eight hours each, a rate of feed of carburizing and control compounds in combination of 300 cubic centimeters per hour, and the point of introduction of the mixture of carburizing and control compounds in advance of and adjacent its first contact with the load as in Fig. 1 indicated; percentages of compounds are by volume:

(*a*) Dipentene 20%, as the carburizing compound, and 80% of denatured ethyl alcohol, yielded a surface concentration of carbon 1.25%, i. e., surface saturation, from top to bottom of the load with a deviation from absolute uniformity of between .01 and .02% carbon; amount of soot formed negligible.

(*b*) 25% dipentene and 75% methyl alcohol, yielded a surface sub-saturation of 1.16% carbon, with a deviation from absolute uniformity of only .01% carbon.

(*c*) Ethyl alcohol, 50%, and glycerine 50% yielded a surface sub-saturation of .45% carbon with a deviation of .015% carbon from absolute uniformity from top to bottom of the load. (Increase in the proportion of glycerine decreases the amount of available carbon.)

Among other convenient mixtures may be noted:

Fusel oil or butyl alcohol or amyl alcohol 50%, with denatured ethyl alcohol, 50%.

Dipentene 25% to 40% with denatured ethyl alcohol 75% to 60%.

Fusel oil 45% with methyl alcohol 55%.

It will be understood that for other depths of load and for conditions other than those attending the carburizing runs above exemplified, the rates of feed of the carburizing and control compounds in combination will in general be greater as the depth of load is greater and the carburizing and control compounds themselves may be different from those above indicated and their proportions may be different.

I disclaim use of bone oil and nitrobenzene.

What I claim is:

1. In a method of carburizing in which there is brought into contact with the load at carburizing temperature a carbonaceous material which is cracked to yield the case-forming carbon, the improvement which consists in maintaining in intimate mixture with said carbonaceous material during cracking thereof a control material comprising a compound or compounds selected from the group consisting of the lighter alcohols of the monohydric type, dihydric and polyhydric alcohols, aldehydes, ketones, dibasic and polybasic acids, and isomers of aforesaid compounds, said materials being present in such predetermined proportions that the cracking of said first-named material is spread over extents of space within the load zone materially greater than in the absence of said control material.

2. A method of carburization to effect saturation at the surface of a load, which comprises passing in contact with the load from one to another limit thereof while at carburizing temperature a carbonaceous material which when yielding case-forming carbon sufficient to saturate the surface of the load throughout the extent thereof between said limits produces excessive soot, and maintaining in intimate mixture with said carbonaceous material a control material comprising a compound or compounds selected from the group consisting of the lighter alcohols of the monohydric type, dihydric and polyhydric alcohols; aldehydes, ketones, dibasic and polybasic acids, and isomers of aforesaid compounds, said control material being present in proportion to said carbonaceous material, to maintain saturation of the surface of the load throughout its extent between said limits with substantial elimination of soot formation at a rate of supply of said carbonaceous material substantially less than that required to produce surface saturation throughout the extent of the load between said limits in the absence of said control material.

3. A method of carburizing to effect a predetermined desired sub-saturation magnitude of carbon concentration in the surface of a load, which comprises passing in contact with the load from one limit to another thereof while at carburizing temperature a carbonaceous material which used alone yields on cracking case-forming carbon, and maintaining in intimate mixture with said carbonaceous material thermally to govern its yield of case-forming carbon a control material comprising a compound or compounds selected from the group consisting of the lighter alcohols of the monohydric type, dihydric and polyhydric alcohols, aldehydes, ketones, dibasic and polybasic acids, and isomers of aforesaid compounds, said control material being present in proportion to said carbonaceous material, to effect a substantially uniform sub-saturation concentration of carbon in the surface of the load substantially throughout its extent between said limits, and bringing said sub-saturation concentration to said predetermined desired magnitude, with substantial uniformity thereof throughout the extent of the load between said limits, by correspondingly changing the rate of supply of said materials.

4. A method of carburizing or controlling the concentration of carbon in the surface of steel, which comprises passing in mixture in contact with the steel and raising them to cracking temperatures, immediately in advance of and adjacent their first contact with the steel, a control material comprising a compound or compounds selected from the group consisting of the lighter alcohols of the monohydric type, dihydric and polyhydric alcohols, aldehydes, ketones, dibasic and polybasic acids, and isomers of aforesaid compounds, and a carbonaceous material yielding carbon on cracking thereof, said control material being present in predetermined proportion to said carbonaceous material to control to predetermined extent the action thereof and the concentration of carbon in the surface of the steel.

5. In the art of carburizing, a method which comprises passing through the load at carburizing temperature and cracking a carburizing material itself yielding carbon at a rate which varies with distance through the load, and spreading the cracking of said carburizing material through the load and slowing the rate of said cracking by maintaining in mixture with

said material during passage through the load a control material comprising a compound or compounds selected from the group consisting of the lighter alcohols of the monohydric type, dihydric and polyhydric alcohols, aldehydes, ketones, dibasic and polybasic acids, and isomers of aforesaid compounds, said control material being present in such proportion, predetermined with respect to the length of path of the mixture through the load, that during concurrent cracking thereof it by absorption of predetermined proportion of total heat available for cracking said materials slows the cracking of said carburizing compound.

6. In the art of carburizing, a method which comprises passing through the load at carburizing temperature and cracking a carburizing material yielding carbon at a rate which varies with distance through the load, and modifying to predetermined extent the carbon-yield/distance characteristic representative of said cracking by maintaining in mixture with said carburizing material a control material comprising a compound or compounds selected from the group consisting of the lighter alcohols of the monohydric type, dihydric and polyhydric alcohols, aldehydes, ketones, dibasic and polybasic acids, and isomers of aforesaid compounds, said control material being present in predetermined proportion to said carburizing material, and yielding case-forming carbon in amount at most insignificant in comparison with that yielded by said carburizing compound.

7. A method of carburizing which comprises raising to cracking temperature immediately in advance of and adjacent their first contact with the load a carburizing material, itself having the characteristic of cracking to yield carbon at a rate which varies with distance through the load, in mixture with a control material for modifying the carbon-yield/distance characteristic, representative of aforesaid cracking, present in predetermined proportion to said carburizing material with effect to modify said characteristic to predetermined extent and itself yielding case-forming carbon in amount at most insignificant compared with that yielded by said carburizing material, said control material comprising a compound or compounds selected from the group consisting of the lighter alcohols of the monohydric type, dihydric and polyhydric alcohols, aldehydes, ketones, dibasic and polybasic acids, and isomers of aforesaid compounds.

8. A method of carburizing which comprises raising to cracking temperature immediately in advance of and adjacent its first contact with the load a carburizing material yielding carbon at a rate which decreases with distance through the load and supplied at a rate yielding a case of surface concentration which decreases with distance through the load, and reducing the slope of the surface concentration/distance characteristic by maintaining in mixture with said carburizing material throughout contact with the load a control material comprising a compound or compounds selected from the group consisting of the lighter alcohols of the monohydric type, dihydric and polyhydric alcohols, aldehydes, ketones, dibasic and polybasic acids, and isomers of aforesaid compounds, said control material being present in such predetermined proportion, and endothermically cracked by absorption of such predetermined proportion of the available heat, that the slope of the carbon-yield/distance characteristic, representative of cracking of the carburizing material, is reduced.

9. As a new composition of matter for heat treatment of a load of steel in respect to concentration of carbon in its surface, a prepared mixture comprising a carbonaceous control material comprising a compound or compounds selected from the group consisting of the lighter alcohols of the monohydric type, dihydric and polyhydric alcohols, aldehydes, ketones, dibasic and polybasic acids, and isomers of aforesaid compounds, and a carbonaceous material yielding carbon on cracking thereof during passage with said control material in contact with the load, said control and carbon-yielding materials being present in the mixture in such definite proportions and so predetermined that the yield of carbon by said second-named material during cracking thereof in progress through the load is substantially prolonged.

10. A method of carburizing or controlling the concentration of carbon in the surface of steel which comprises passing dipentene in contact with the steel at temperature effecting cracking thereof, and controlling the rate of cracking by denatured ethyl alcohol in mixture with the dipentene while cracking.

11. A method of carburizing or controlling the concentration of carbon in the surface of steel which comprises passing fusel oil in contact with the steel at temperature effecting cracking thereof, and controlling the rate of cracking by denatured ethyl alcohol in mixture with the fusel oil while cracking.

12. A method of carburizing or controlling the concentration of carbon in the surface of steel which comprises passing dipentene in contact with the steel at temperature effecting cracking thereof, and controlling the rate of cracking by methyl alcohol in mixture with the dipentene while cracking.

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