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HEAT TREATMENT OF METALS

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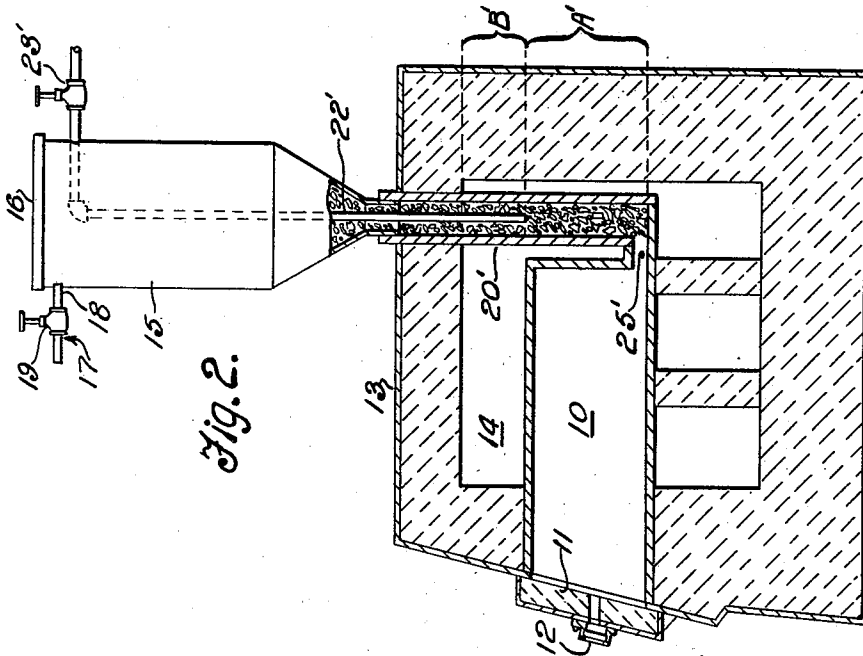


Fig. 2.

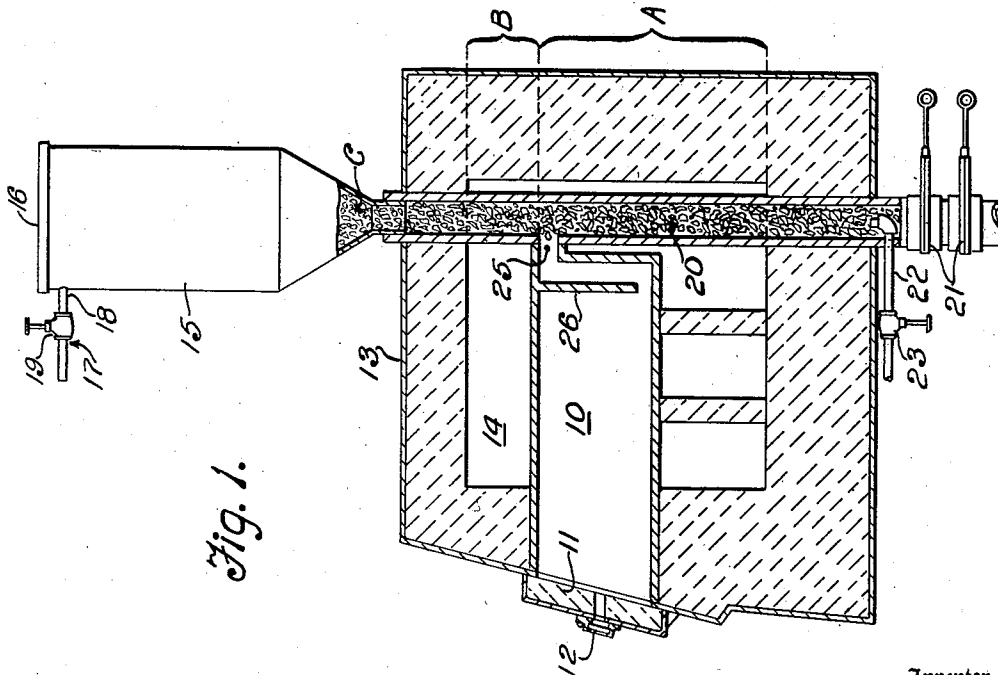


Fig. 1.

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HEAT TREATMENT OF METALS

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Continuation of application Serial No. 227,487, August 30, 1938. This application March 5, 1940, Serial No. 322,321

9 Claims. (Cl. 148—16)

This application is a continuation of my application, Serial No. 227,487, filed August 30, 1938. Reference is also made to my Patent No. 2,188,275 dated January 23, 1940, wherein the apparatus herein disclosed is claimed.

The present invention has for its object to provide for the heat treatment of steel articles and molybdenum high speed tool steel in particular in a manner to avoid decarburization, scaling and hydrogen sorption.

The heat treatment of molybdenum high speed steel presents difficulties that are not encountered in the heat treatment of other high speed steels. Thus, whereas tungsten high speed steel can be clean hardened with practically no decarburization in an atmosphere resulting from the partial combustion of hydrocarbon gases, molybdenum high speed steel must be coated with a refractory material such as boric oxide, water glass or the like, as otherwise it will become decarburized. It is accepted that tungsten high speed steel is not decarburized in such an atmosphere due to the formation of an impervious stable oxide film over the surface of the article, this film being initially formed at low temperatures in the preheat furnace and remaining throughout the high heat furnace treatment. In the case of molybdenum high speed steel, however, such a protective oxide film cannot be maintained at heat treating temperatures since molybdenum oxide is extremely volatile at heat treating temperatures as is readily observed during forging, a bluish white fume resembling cigarette smoke coming off.

The nearer such an atmosphere is regulated to a non-oxidizing constituency, i. e., by increasing gas-air ratio, the more pronounced is the decarburization of the work. Consequently such atmospheres are limited to the production of a minimum degree of oxidation consistent with maximum allowable decarburization on such steels as form self-protecting oxide films at the particular heat treating temperature.

In the course of my experiments leading up to the present invention, I heated specimens of molybdenum high speed in an atmosphere of ordinary charcoal gas but without satisfactory results. I also made numerous tests using tank gases including nitrogen, hydrogen, ammonia, propane, etc. Mixtures of 10% hydrogen and 90% nitrogen, which were deoxidized by passing over iron filings at a temperature between 600° and 700° F. and dehydrated by activated alumina, decarburized molybdenum high speed steel at heat treating temperatures. Tank hydrogen alone similarly deoxidized and dehydrated also

caused decarburization and, furthermore, to a greater degree than in the case of the mixed gases. Tank nitrogen dried and deoxidized as above did not decarburize the steel but the specimens were found to be etched with a crystalline pattern resulting apparently from a slight oxidation on heating followed by vaporization of the resulting molybdenum oxide at high temperature. It became evident, therefore, that an inert gas, such as commercial nitrogen, could not be used for this purpose because it cannot be obtained sufficiently free from oxidizing gas even if it could be maintained in such a condition during use and also that hydrogen was an undesirable reducing gas for mixing with the inert nitrogen. These observations were confirmed by the results obtained when using ammonia.

As a result of my experiments, I have discovered and this forms the basis of the present invention that molybdenum high speed steel can be successfully heat treated in an atmosphere containing CO, CO₂, N₂ and H₂ provided that the H₂ content is kept down to a very low limit, namely, to an amount not in excess of three one-hundredths (.03) partial pressure in atmospheres. In general it may be said that for best results, the protective atmosphere should be substantially free from water vapor; that the relative proportions of carbon monoxide and carbon dioxide should be such as to be in equilibrium with the steel at the prevailing temperature; that the hydrogen content expressed in partial pressure in atmospheres should be less than three one-hundredths (.03), and that the nitrogen content expressed in partial pressure in atmospheres should be less than eighty-five one-hundredths (.85).

It is known from the work of others, and notably Takahashi (see the article, in English, entitled "On the equilibrium between austenite and carbon oxides" by Genske Takahashi, published in the Science Reports of Tohokii Imperial University, Sendi, Japan, vol. XV.), what the ratio of the square of the partial pressure in atmospheres of carbon monoxide divided by the partial pressure in atmospheres of carbon dioxide should be to be in equilibrium with steel of any particular carbon content at any particular temperature. Thus, for a steel at a temperature of 1500° F. and having a carbon content of eighty-ninths per cent (.80%), the said ratio is in the neighborhood of 12 whereas for the same steel at a temperature of 220° F., the ratio is in the neighborhood of 100.

This is only another way of saying that at the

higher heat treating temperatures it is necessary to have an atmosphere practically free from CO₂ in order to avoid decarburization in the absence of scale. Tables containing this data are well known and widely used in the art. By referring to such tables it is possible to ascertain very quickly what the relative proportions of CO and CO₂ should be to be in equilibrium at various temperatures and to determine whether or not these components will be decarburizing, neutral or carburizing when in contact with a high carbon steel at the temperatures selected.

At this point it may be stated that molybdenum high speed steel contains about 9% molybdenum, 4% chromium, 1% vanadium and .78% carbon and that such steel is today recommended to be hardened at from 2150° to 2250° F., the usual temperature being 2200° F. Consequently at a temperature in the neighborhood of 2200° F., the relative proportions of CO and CO₂ expressed in partial pressures in atmospheres should be such that the ratio of

$$\frac{(CO)^2}{CO_2}$$

is in the neighborhood of 100. At the lower pre-heating temperatures, the said ratio would of course be lower but not lower than 10 for a temperature of 1500° F., this being the temperature at which the steel is allowed to soak thoroughly before being raised to the high heat temperature.

A protective atmosphere as above described does not form an oxide film on the work nor does it depend on the protection of such a film for the prevention of decarburization. Furthermore, the low hydrogen content precludes harmful hydrogen sorption, i. e., diffusion and absorption of hydrogen into the metal being treated. Moreover, I have found that such a furnace atmosphere does not place a time limit at which the work may be held at temperature as in the case when using other atmospheres since, as I have found, the work may be left for periods of several hours without decarburizing or scaling. Obviously this degree of protection may well be the basis of a new order of physical properties of heat treated steels.

The present invention also provides a simple and practical method and apparatus for making the said protective atmosphere. Briefly stated, the protective atmosphere is produced by passing an oxygen-containing gas low in hydrogen or hydrogen compounds (this gas being hereinafter sometimes termed "base gas") through a bed or column of externally heated carbonaceous material which has been so conditioned by heat treatment as to be substantially devoid of hydrogen or hydrogen-containing compounds whereby the amount of hydrogen in said reaction products is substantially dependent on the amount of hydrogen or hydrogen compounds initially contained in said base gas, the temperature of said carbonaceous material and the rate of flow of the base gas being so controlled as to produce the required or desired relative proportions of CO and CO₂ to insure that the ratio of

$$\frac{(CO)^2}{CO_2}$$

expressed in partial pressures in atmospheres shall be non-decarburizing with respect to the steel at the prevailing heat treating temperature. The raw carbonaceous material may be charcoal or coke or other equivalent material, charcoal being preferred. The choice of base gas will be determined largely by its relatively low content

of hydrogen or hydrogen compounds and by its nitrogen content. Included in such base gases are air, dried flue gas, dried ammonia combustion products, and special producer gas. Various mixtures of these gases may, of course, be used to arrive at the desired nitrogen content in the final reaction products.

In the accompanying drawing forming part of this specification, I have shown two forms of apparatus that may be used in the practice of the present invention. Fig. 1 is a vertical section of a heat treating furnace embodying a built-in gas generator designed to operate on what I call the "counterflow" principle. Fig. 2 is a vertical sectional view of the same kind of a heat treating furnace but embodying a built-in gas generator designed to operate on what I call the "parallel flow" principle.

Like reference numerals indicate like parts in the two views.

In both views, the heat treating furnace is shown as of the muffle type. 10 indicates the muffle, the same being provided at its front end with the usual door 11 through which the work to be heat treated may be placed in and removed from the muffle. The door is shown as provided with a glass-covered sight hole 12 to permit visual inspection of the work in the muffle. The furnace setting for the muffle is generally indicated at 13, the same comprising a furnace chamber 14 which surrounds the muffle for uniformly heating the latter. As is customary in muffle furnaces, burners (not shown) fire into the furnace chamber 14 and said burners are controlled by temperature control apparatus (not shown) for controlling the temperature of the muffle 10.

15 indicates a hopper or magazine adapted to contain the carbonaceous material C hereinbefore referred to. The top of the hopper will normally be kept closed by a cover 16. For reasons presently appearing the hopper is provided with a vent generally indicated at 17, the same being shown as comprising a pipe 18 provided with a hand valve 19 for controlling the effective discharge area of the vent.

In the form of apparatus shown in Fig. 1, the hopper 15 delivers the carbonaceous material to a vertical retort 20 positioned within the furnace chamber 14 to the end that it may be heated to the same, or substantially the same, temperature as the muffle 10. The retort is shown as long enough to extend downwardly out of the furnace chamber with its lower end normally closed by any suitable removable closure, such as gate valves 21, to permit removal of ash. Leading into the lower end of the retort is a pipe 22 through which the base gas hereinbefore mentioned is delivered to the retort for upward flow through the heated carbonaceous material. Said pipe leads from a source of supply of such gas and is provided with a flow adjusting valve 23.

A gas connection 25 is provided between the muffle 10 and the retort 20. For reasons presently appearing, said connection is a substantial distance upwardly from the discharge end of the gas pipe 22 and is also a substantial distance downwardly from the top of the furnace chamber 14. With respect to the muffle, said gas connection 25 is shown as at the upper rear corner thereof but inasmuch as it is desirable that the gas enter the muffle proper near the floor thereof, there is provided in the muffle a depending baffle 26 which serves to direct the gas downwardly.

In the form of apparatus shown in Fig. 2, the retort to which the hopper 15 delivers is indicated

at 20', it being noted that this retort, like the retort 20 in Fig. 1, is within the furnace chamber wherein the muffle is positioned as a consequence of which the retort will be heated to the same or substantially the same temperature as the muffle. The gas connection between the muffle and the retort is indicated at 25'. The pipe through which the base gas is supplied to the retort is indicated at 22', and it will be noted that this pipe extends downwardly into the retort above and terminates a substantial distance above the gas connection 25'. Ash resulting from the combustion of the carbonaceous material may be removed from the lower end of the retort by way of the gas connection. However, it will be readily appreciated that the lower end of the retort might well be extended downwardly below the gas connection to form a receptacle from which ash may be withdrawn.

In Fig. 1, the retort 20 may be considered as comprising two zones A and B. Zone A is the gas making portion of the retort and zone B is the place where the carbonaceous material is conditioned before moving into zone A. In Fig. 2, the zones which correspond to the zones A and B in Fig. 1 are indicated at A' and B' respectively.

For temperatures above 1850° F. the retort in both forms of apparatus will be made of a heat-conducting refractory which preferably will be silicon carbide. For temperatures below 1850°, it may be made of heat-resisting alloy.

To produce the protective gas with the gas generator shown in Fig. 1, the procedure is substantially as follows. Having made sure that the hopper vent 17 is open, the valve 23 in the base gas supply pipe 22 is opened to such degree that considerably more base gas will always be supplied to retort 20 than is required to meet the requirements of the muffle 10 to the end that some of said gas shall always flow through zone B (and finally out through the hopper vent 17) in a direction opposed to the down-coming carbonaceous material C whereby to prevent the volatiles given off by the heated carbonaceous material in zone B from contaminating the reaction products produced in zone A. The same procedure is followed with the gas generator shown in Fig. 2, it being understood that some of the base gas from the discharge end of the supply pipe 22' will flow upwardly through zone B'. By thus continuously purging the zone (B or B') where the carbonaceous material is preheated, it will be readily appreciated that the hydrogen content of the reaction products entering the muffle by way of the gas connection 25 (25') may be readily controlled within the limits hereinbefore mentioned by utilizing a base gas whose content of hydrogen or hydrogen-containing compounds is known.

The relative proportions of CO and CO₂ in the products of reaction are a function of the temperature to which the carbonaceous material is heated and by maintaining the retort at the same or substantially the same temperature as the muffle the ratio of

$$\frac{(CO)^2}{CO_2}$$

expressed in partial pressures in atmospheres will be such as to be neutral or slightly carburizing to the steel. Although for simplicity of construction it is preferred that the retort be located in the furnace chamber which serves to heat the muffle, nevertheless the retort and the gas connection between the retort and muffle may be otherwise heated to the required temperature.

In the heat treatment of tool steel it is customary to employ two furnaces, one of which is usually referred to as the "preheat" furnace and the other as the "high heat" or "super heat" furnace. In the case of molybdenum high speed steel the temperature of the preheat furnace will ordinarily be maintained at a temperature of about 1550° F. (the work being allowed to soak thoroughly at this temperature) and the super heat furnace at a temperature of about 2200° F. As an indication of the difference in gas composition of the reaction products entering the muffle from the zone A (A') and those issuing from the hopper vent when the retort is maintained at the two temperatures mentioned and when the base gas is low pressure atmospheric air, the following examples are given:

EXAMPLE No. 1.—Retort at 1550° F.

	Hopper gas	Muffle gas
	Percent	Percent
CO ₂	3.6	0.7
O ₂	0.0	0.0
CO.....	28.7	33.1
H ₂	7.4	2.1
CH ₄	0.0	0.0
N ₂	Balance	Balance

EXAMPLE No. 2.—Retort at 2200° F.

	Hopper gas	Muffle gas
	Percent	Percent
CO ₂	3.8	0.1
O ₂	0.0	0.0
CO.....	30.6	34.5
H ₂	7.7	1.2
CH ₄	0.0	0.0
	Balance	Balance

The so-called "hopper gas," that is to say, the gas issuing from the vent 17 is entirely unsuited for use as a protective atmosphere for molybdenum high speed steel. The so-called "muffle gas," however, that is to say, the gas which enters the muffle 10 from the zone A(A') of the retort will protect not only molybdenum high speed steel but also other high speed steels and, in fact, steels generally against decarburization, scaling and hydrogen sorption. In this connection it may be stated that furnace atmospheres produced as herein described are applicable to many heating operations carried out on metals, including and especially, annealing, normalizing, preheating, hardening, tempering, brazing, melting, forging, etc.

From the foregoing, it will be seen that although the invention is particularly concerned with a protective atmosphere for molybdenum high speed steel, nevertheless an atmosphere produced in accordance with the present invention is useful in the heat treatment of metals generally. Consequently, I wish it to be understood that no limitations are intended except as expressed in the appended claims.

What I claim is:

1. The method of heat treating articles of steel in a furnace chamber which comprises maintaining a retort for carbonaceous material at a temperature substantially the same as that of said chamber, said retort having an offtake delivering to said chamber and having an opening remote from said offtake for the inflow of carbonaceous material from an extraneous source of supply and for the outflow of volatiles and vapors ordinarily given off by the incoming ma-

terial on being heated, delivering to said retort at a point remote from said opening a sufficient volume of a reactive gas to insure simultaneous outflow of gas through the said opening and
 5 offtake whereby to insure that the gas which flows into said chamber by way of said offtake shall be substantially devoid of the said volatiles and vapors, the said reactive gas consisting essentially of components which will react with the
 10 heated carbonaceous material to produce oxides of carbon to the substantial exclusion of hydrogen components.

2. The method of heat treating articles of steel in a furnace chamber which comprises maintaining a body of carbonaceous material in an externally heated retort at a temperature not less than that of said chamber, said retort having an offtake delivering to said chamber and having
 15 an opening remote from said offtake for the inflow of carbonaceous material from an extraneous source of supply and for the outflow of volatiles and vapors ordinarily given off by the incoming material on being heated, delivering to said retort at a point remote from said opening a sufficient
 20 volume of a reactive gas to insure simultaneous outflow of gas through the said opening and offtake whereby to insure that the gas which flows into said chamber by way of said offtake shall be substantially devoid of the said volatiles and
 30 vapors, the said reactive gas consisting essentially of components which will react with the heated carbonaceous material to produce oxides of carbon to the substantial exclusion of hydrogen components, and the gas which flows to the
 35 furnace chamber from said retort being maintained during its flow at a temperature not less than that of said chamber.

3. The method of supplying to a furnace chamber wherein steel articles are placed for heat
 40 treatment an atmosphere comprising oxides of carbon in substantial equilibrium with the steel at the temperature of said chamber, said oxides being made by heating carbon in the presence of air in a retort in gas connection with said
 45 chamber and being substantially devoid of the volatile impurities given off by ordinary commercial carbon when it is first heated, which method comprises maintaining said retort and chamber at substantially the same temperature,
 50 feeding said carbon into said retort from an external source of supply, continuously preventing said impurities from flowing to said gas connection by continuously drawing off said impurities against the incoming carbon, and flowing
 55 said air into the retort at a point where the carbon is substantially devoid of said impurities.

4. The method of heat treating steel articles in a furnace chamber that is in gas connection with a retort for carbonaceous material, which
 60 method comprises maintaining said retort and chamber and gas connection at substantially the same temperature, maintaining a supply of said material in said retort by feeding the material thereto from an extraneous source of supply, continuously preventing volatile impurities given off
 65 by said material as it becomes heated from flowing to said chamber by way of said gas connection by continuously drawing off gas from the retort against the incoming carbonaceous material, and delivering to said retort at a point where
 70 said material is substantially devoid of said impurities an oxygen containing gas to produce reaction products consisting essentially of carbon monoxide for flow to said chamber by way of said gas connection.

5. The method of supplying to a furnace chamber wherein metal articles are placed for heat treatment an atmosphere consisting essentially of oxides of carbon substantially devoid of the volatile impurities given off by ordinary commercial charcoal when it is first heated, said oxides being made by heating said charcoal in an externally heated retort in the presence of air, which method comprises feeding the charcoal into the retort from an external source of supply, continuously preventing said impurities from flowing to said gas connection by continuously drawing off gas from retort against the incoming charcoal, and flowing said air into the retort at a point where the charcoal is substantially devoid
 10 of said impurities.

6. The method of heat treating articles of high speed steel in a furnace chamber which comprises maintaining a retort for carbonaceous material and said chamber at a temperature in the neighborhood of 2200° F., said retort having an offtake delivering to said chamber and having an opening remote from said offtake for the inflow of carbonaceous material from an extraneous source of supply and for the outflow of volatiles and
 25 vapors ordinarily given off by the incoming material on being heated, delivering to said retort at a point remote from said opening a sufficient volume of a reactive gas to insure simultaneous outflow of gas through the said opening and off-
 30 take whereby to insure that the gas which flows into said chamber by way of said offtake shall be substantially devoid of the said volatiles and vapors, the said reactive gas consisting essentially of components which will react with the heated
 35 carbonaceous material to produce oxides of carbon to the substantial exclusion of hydrogen components.

7. The method of supplying to a furnace chamber wherein articles of high speed steel are placed
 40 for heat treatment an atmosphere comprising oxides of carbon in substantial equilibrium with the steel at the temperature of said chamber, said oxides being made by heating carbon in the presence of air in a retort in gas connection with said
 45 chamber and being substantially devoid of the volatile impurities given off by ordinary commercial carbon when it is first heated, which method comprises maintaining said retort and chamber at a temperature in the neighborhood of 2200°
 50 F., feeding said carbon into said retort from an external source of supply, continuously preventing said impurities from flowing to said gas connection by continuously drawing off said impurities against the incoming carbon, and flowing
 55 said air into the retort at a point where the carbon is substantially devoid of said impurities.

8. The method of heat treating steel articles in a furnace chamber that is in gas connection with a retort for carbonaceous material, which method
 60 comprises maintaining said retort and chamber and gas connection at a temperature not less than 1550° F., maintaining a supply of said material in said retort by feeding the material thereto from an extraneous source of supply, continuously preventing volatile impurities given off
 65 by said material as it becomes heated from flowing to said chamber by way of said gas connection by continuously drawing off gas from the retort against the incoming carbonaceous material, and delivering to said retort at a point where said material is substantially devoid of said impurities an oxygen containing gas to produce reaction
 70 products consisting essentially of carbon monoxide for flow to said chamber by way of said gas connection.

oxide for flow to said chamber by way of said gas connection.

5 9. The method of supplying to a furnace chamber wherein metal articles are placed for heat treatment an atmosphere consisting essentially of oxides of carbon substantially devoid of the volatile impurities given off by ordinary commercial charcoal when it is first heated, said oxides being made by heating said charcoal to a temperature of from 1550° to 2200° F. in an exter-

nally heated retort in the presence of air, which method comprises feeding the charcoal into the retort from an external source of supply, continuously preventing said impurities from flowing to said gas connection by continuously drawing 5 off gas from retort against the incoming charcoal, and flowing said air into the retort at a point where the charcoal is substantially devoid of said impurities.

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