May 4, 1954 P. F. W. HOWARTH 2,677,667

PROCESS FOR THE REVIVIFICATION
OF SPENT CARBONACEOUS MATERIAL
Filed March 19, 1951

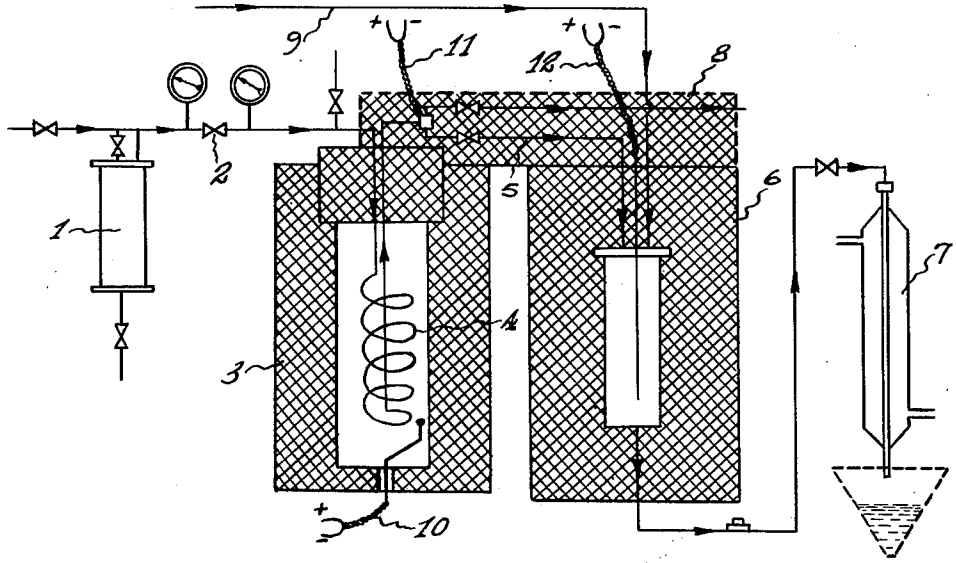


FIG. 1

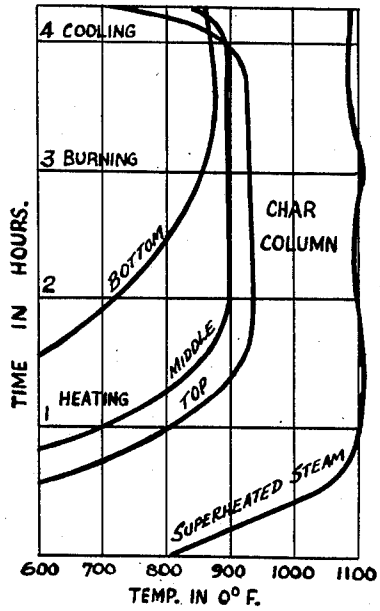


FIG. 2

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Patented May 4, 1954

2,677,667

UNITED STATES PATENT OFFICE

2,677,667

PROCESS FOR THE REVIVIFICATION OF SPENT CARBONACEOUS MATERIAL

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Application March 19, 1951, Serial No. 216,348

3 Claims. (Cl. 252—420)

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This invention relates to an improved process for the revivification of adsorbent material of a carbonaceous nature, such as bone char, used to remove colouring matter from liquors in various refining processes such as, for example, the refining of sugar.

In the past revivification of bone char has been carried out by burning in Scotch kilns. This produces an irregularly treated material, part of the char being overburnt and part underburnt. Presumably this is due to the quite severe temperature differences throughout the kilns. Such temperature differences are probably due to the poor thermal conductivity of the char, which has been given as 0.09 B. t. u. feet^{-1}, hour^{-1}, °F.$^{-1}$. This low thermal conductivity is of the same order as that of asbestos. The irregular performance of the Scotch kilns may also be due to the low thermal diffusivity of bone char, being only 0.0080 feet^2 hours^{-1}. In a material of such low thermal diffusivity it takes a long time to smooth out any local temperature irregularities.

Numerous attempts have been made to overcome the disadvantages of the Scotch kiln treatment by supplying heat internally to spent char by treating the char with a heated gas or vapour. Exemplary of these is the Herreshoff furnace which uses direct heating by combustion gases from an oil burner.

On the industrial scale one of the most convenient of such heat transfer gases is superheated steam. It is conveniently available and has a suitably high specific heat so that it can be made to transfer heat efficiently to the surface of each individual grain of char. However, apart from this highly desirable physical property superheated steam has a specific chemical reaction with carbonaceous matter which may, or may not, be of assistance in reactivating bone char.

The use of superheated steam to reactivate bone char has been made the subject of a number of patents. However, while it appears that the steam reactivation process offers, at least on paper, some considerable advantages over the normal process, it is not at all clear from the literature whether such advantages may be realised without complications due to undesirable side reactions.

The object of the present invention, therefore, is to provide a process of revivifying bone char and similar spent carbonaceous adsorptive materials with superheated steam which process is substantially free of undesirable side reactions.

It is also an object of the present invention to provide a process of revivifying bone char and similar materials without substantially impairing the desirable characteristics of the material.

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According to the present invention a process for revivifying spent carbonaceous adsorptive materials comprises treating the spent material with superheated steam and thereafter treating the material with a gas containing carbon dioxide and thoroughly mixing the treated material before reusing.

The method of revivification according to the process of the present invention may be conveniently carried out in apparatus such as that shown diagrammatically in Fig. 1 of the accompanying drawing. However it should be understood that the invention is not limited to the use of the particular apparatus disclosed herein. Any other suitable form of apparatus may be used if desired.

Saturated steam at 60 p. s. i. g. pressure is passed into a trap 1 and then through a reducing valve 2 into a superheater 3 consisting of an Inconel tube 4 in an electric furnace. The superheated steam then passes along line 5 to a revivifying vessel 6 containing the material to be treated and from the revivifying vessel to a condenser 7.

The revivifying vessel 6 consists of a fixed outer shell fitted with an outlet pipe at the bottom and a removable lid at the top. A removable inner vessel of lighter construction holds the material to be treated. The top of this inner vessel is open and the bottom perforated to retain the material while allowing the steam to pass through. The small annular space between the walls of this inner vessel and the outer shell are plugged so that steam cannot by-pass the bed.

A by-pass line 8 to divert steam not properly heated is provided. A line 9 to feed cool steam or other gas or vapour to the revivifying vessel is also provided. The superheater 3, the superheated steam line 5 and the revivifying vessel are closely lagged and provided with thermocouples 10, 11 and 12 respectively. The rate of steam flow is measured by the rate of condensation in condenser 7.

The revivifying vessel 6 is heated only by the superheated steam and Fig. 2 of the accompanying drawing gives, during a typical run, a time record of the temperature at three different points in the vessel—near the bottom, near the centre and near the top—the traverse being along the axis of the vessel.

In carrying out the process of the present invention superheated steam at an initial temperature of 800° F. is passed into the revivifying vessel packed with the spent material. The temperature is then raised as rapidly as possible to 1100° F. and maintained there for the duration of the treatment. Under the influence of this heated

steam the material, in at least the major part of the reactivating vessel, is maintained at 900° F. for the greater part of the cycle. It will be evident from a consideration of Fig. 2 that there is some tendency for the low portion of the vessel to be cooler with the result that the material in this section tends to be underburnt. After the treatment with superheated steam is complete the material is cooled by admitting cool saturated steam to the vessel. The freshly revivified material is then packed in an open tower and gases containing CO_2 passed up through the material until CO_2 can be detected in the gases emerging from the top of the tower. The material so treated is then thoroughly mixed before reusing.

Alternatively the treated material may be cooled by passing gases containing CO_2 into the revivifying vessel instead of the cool saturated steam.

In the cycle illustrated in Fig. 2 the reaction vessel was maintained at a temperature of approximately 900° F. for about four hours. The maintenance of these particular time-temperature curves is dependent on the rate of steam flow. The curves as shown in Fig. 2 are obtained when the steam flow has a linear velocity of 1 foot/sec. at a pressure of 15 p. s. i. g.

In carrying out the process of the present invention the rate of steam flow is so adjusted that the central temperature of the material being treated is brought to a temperature of 900° F. as quickly as possible and maintained at that temperature for the duration of the treatment.

While the preferred operating temperature of the superheated steam revivification process is approximately 900° F. the process may be carried out at any temperature within the range 800°–1100° F.

The time of treatment of the material with the superheated steam varies with the temperature at which the treatment is effected, the higher the temperature the shorter the duration of treatment. The duration of treatment is also dependent on the nature of material i. e. whether it is only partially spent or whether it is completely spent. Tests are made at appropriate intervals to determine the relative colour adsorptive capacity. When this reaches a predetermined level the steam treatment is discontinued.

Any gas containing a suitable proportion of carbon dioxide may be used to treat or cool the supersaturated steam treated char. Flue gases, containing 8–20% carbon dioxide, may be conveniently used. The proportion of carbon dioxide, however, is not critical and gases containing much more or much less carbon dioxide may be used satisfactorily.

Material treated with flue gases in accordance with the present invention absorbs carbon dioxide very rapidly, so rapidly indeed that the effective pH near the gas inlet is brought down to about pH7 before any CO_2 reaches the top of the tower. However, despite the unevenness of the pH throughout the bed of material, suitable mixing gives a material of satisfactory characteristics.

The following is an example of the revivification of bone char in accordance with the invention.

EXAMPLE I

4 lbs. of exhausted char from a sugar refinery were packed in a reactor vessel of 4 inches internal diameter fitted with a central thermocouple well. Steam superheated to 1100° F. was admitted at such a rate that the velocity through the bed was 2 feet per second. The temperature rose rapidly to 850° C. and was maintained between that temperature and 900° C. for 30 minutes by throttling back the rate of steam flow to 1 foot per second. The char was then cooled in a stream of dry steam, treated with a current of pure CO_2 at a flow rate of 0.5 foot per second for 3½ minutes, and finally mixed by transference to another vessel. The resultant revivified char which had a pH of 10.9 before treatment with CO_2 had now a pH of 7.8, contained 3.75% $CaCO_3$, and gave a very satisfactory performance in the miniature cistern test.

In order to determine whether or not the process of revivifying bone char in accordance with the present invention resulted in a progressive deterioration of the known characteristics, char, which had been reactivated by treatment with superheated steam followed by treatment with flue gas which restored the effective pH to the normal value for fresh char, was subjected to a series of cyclic treatments of exhaustion with raw sugar liquors followed by regeneration.

EXAMPLE II

20 lbs. of exhausted char were revivified in four separate batches according to the technique given in Example I, but at a higher temperature (namely a maximum of 1,000° F.). The four batches were thoroughly mixed and 4 lbs. were put away for testing. The remaining 16 lbs. were exhausted by treatment with raw liquor until a distinct caramel colour ran through the char. The char was then washed, dried and regenerated according to the technique above. The different batches were mixed and 4 lbs. again placed on one side and the rest exhausted. In this way samples were obtained of char which had passed through up to five cycles of exhaustion and regeneration.

Samples of the revivified char were taken after each revivification, freed from iron scale and ground to dust and then analysed chemically. The properties of the different samples are set out below in Table I.

Table I

CHANGES IN THE PROPERTIES OF CHAR ON REPEATED STEAM REVIVIFICATION FOLLOWED BY NEUTRALIZATION WITH CARBON DIOXIDE

Cycle No.	Relative Adsorptive Capacity for Colors in Raw Liquor	Relative Adsorptive Capacity for Ash in Raw Liquor	Relative Friability	pH		Chemical			
				Char	Final Liquor	Carbon	$CaCO_3$	Ca S.	$CaSO_4$
Normal	100	100	100	8.4	8.7	11.24	3.96	0.16	0.52
1	97	97	94	8.2	8.4				
2	104	96	92	8.8	8.5				
3	100	94	100	8.8	8.7	10.61	3.28	0.07	0.45
4	139	131	102	8.3	8.6				
5	148	123	103	8.5	8.5	9.35	3.28	0.04	0.48

It will be seen that while there is slight decrease in the absorptive capacities on the first steam regenerations, there is a pronounced increase in adsorptive capacities in the later cycles. As far as the relative friabilities of the chars are concerned no significant change appears to occur. On the side of chemical analysis no significant changes occur other than the desirable decrease in the CaS content, and a relatively smaller but nevertheless significant decrease in the carbon content of the char. This decrease in the carbon content may even be associated with the increase in the absorptive capacities. The original char used in these tests apparently contained a little too much carbon. There is no deleterious effect on the pH of the char or the liquor running therefrom.

The repeated cycles of reactivation by the treatment described above, alternating with exhaustion by raw sugar liquor results in a progressive increase in activity which appears to be associated with a progressive decrease in the carbon content. This particular action of steam on char is reminiscent of its action in the production of gas-absorbed activated carbon. The superheated steam appears to selectively oxidise those carbonaceous constituents of low adsorptive capacity leaving those of higher adsorptive capacity.

To illustrate the effectiveness of the treatment with gases containing carbon dioxide bone char was subjected to treatment with supersaturated steam only, and at various temperatures. The chars thus obtained were then analysed in accordance with the following analytical methods:

The effective char pH was measured by extraction with 1% calcium acetate solution using Wayne's method; the char was analysed for carbon, silica, calcium sulphate, ferric oxide, calcium sulphide, calcium carbonate, calcium phosphate and for organic matter; the friability of the char was determined and so was the intensity of colour extracted by boiling for one minute with 2.5% caustic soda solution. In addition the decolourizing efficiency was determined by a miniature cistern test. In this test the adsorptive power of the char for caramel colours was recorded in terms of the volume of fine liquor delivered from the char bed when a certain definite amount of colour had been developed. Such a test is of the form of the usual "break-point" tests used in examining the adsorptive properties of gas absorbent carbons. A similar "break-point" test was applied to the ash content of the liquor running off the char. A raw liquor, of standardized colour and ash content was passed at a standard rate over a bed of the treated char. The volume of liquor delivered was noted both when the colour and the ash content of the effluent had reached predetermined values.

The relative friability of the char was determined by means of a test in which the char was treated in a mill for a standard time and the fines produced were weighed. The higher the weight of fines the more friable the char. Relative figures were obtained by expressing the friability of the initial untreated char for any given set of determinations, as one hundred.

The properties of the chars so treated and analysed are set out below:

The first sample of spent char to be examined was treated at 900° F. for half an hour. The char obtained was extremely alkaline not only in the sense of having a high pH but also in requiring a large amount of acid to bring it to neutrality.

The char obviously contained much free calcium oxide. It had evidently been treated at too high a temperature.

The char treatment temperature was then dropped to 800° F., time of treatment again being half an hour. The result of this treatment was still highly alkaline and in addition gave a distinct colour reaction on the caustic soda treatment. It thus appears that while considerable $CaCO_3$ had been burnt to CaO there still remained incompletely decomposed organic matter in the char. In other words features symptomatic of both "underburning" and "overburning" were present.

In further runs the temperature of treatment was reduced to 680° F. In this instance the effective pH of the resultant "treated" char was normal, but, as expected, the caustic soda "color" was abnormally high. Prolonged treatment at this same temperature tended to raise the effective char pH without appreciably reducing the colour of the caustic soda extract.

When such alkaline char is used for the treatment of raw sugar liquors the CaO is dissolved in the liquor, some sugars are destroyed and changed into saccharinic acids with the result that the ash content of the liquor is increased and the char bed permanently loses some of its $CaCO_3$. Successive treatment of char by exhaustion in the miniature cistern and revivification in steam to a satisfactory NaOH color test showed an alarming cumulative drop in the $CaCO_3$ content of the char as indicated in Table II.

Table II

CUMULATIVE LOSS OF $CaCO_3$ IN STEAM REVIVIFIED CHAR

Char	Percent $CaCO_3$
Original	4.6
After one cycle	2.7
After two cycles	1.5

The formation of free lime in steam revivified char, leading to high alkalinity, is of course due to the dissociative reaction

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

The treatment of char with supersaturated steam without the successive treatment with carbon dioxide also reduces the calcium sulphide content, which undergoes the same type of decomposition with formation of calcium oxide and elimination of H_2S

$$CaS + H_2O \rightleftharpoons CaO + H_2S$$

and there is similar evidence that this loss would be cumulative over repeated regenerations. Some figures showing this progressive loss are given in Table III.

Table III

CUMULATIVE LOSS OF CaS IN STEAM REVIVIFIED CHAR

Char	Percent CaS
Original	.16
After one cycle	.12
After three cycles	.07
After five cycles	.04

In contradistinction to $CaCO_3$, the substance CaS is a most undesirable constituent of char from the point of view of the sugar refiner and this

rapidly cumulative loss by steam revivification is a point in favour of this method.

With regard to its adsorptive properties steam revivified char proved at least comparable to ordinary char.

It will be evident from the above that the treatment of bone char with superheated steam results in (1) an undesirable reduction in the $CaCO_3$ content of the char, and (2) a desirable reduction in the CaS content of the char. The successive treatment of the steam treated char with gases containing carbon dioxide effectively restores the $CaCO_3$ content and adjusts the effective pH to a satisfactory level.

The term "spent adsorptive carbonaceous material" as used in the description and claims refers to carbonaceous material such as activated charcoal, bone char or the like, the adsorptive capacity of which has been exhausted by use in a chemical refining process, such as the clarification of raw sugar liquors.

I claim:

1. A process for the revivification of spent carbonaceous adsorptive material which comprises passing superheated steam at a temperature within the range of 800° F.–1100° F. through the spent material for 3–4 hours, cooling the material, passing gases containing carbon dioxide up through the material until the pH of the material is approximately 7 and the $CaCO_3$ content of the material is substantially equivalent to that of the original carbonaceous adsorptive material and thoroughly mixing the treated material.

2. A process for the revivification of spent carbonaceous adsorptive material which comprises passing superheated steam at a temperature within the range of 800° F.–1100° F. through the spent material until a sample of the material gives a substantially negative colour reaction on boiling for one minute with 2.5% caustic soda solution, cooling the material, passing gases containing carbon dioxide through the material until carbon dioxide can be detected in the gases emerging from the material, and thoroughly mixing the so-treated material, which has a $CaCO_3$ content substantially equivalent to that of the original carbonaceous adsorptive material.

3. A process for the revivification of spent bone char which comprises passing superheated steam through the bone char so that the temperature thereof is maintained at approximately 900° F. and until a sample gives a substantially negative dilute caustic soda colour, cooling the bone char, passing flue gases containing 8–20% of carbon dioxide through the bone char until carbon dioxide can be detected emerging from the bone char thereby restoring the $CaCO_3$ content of the bone char to substantially the same level as that of the original bone char and thoroughly mixing the so-treated bone char.

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