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THE DECARBONIZATION OF BONE-BLACK.[1]

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THE chief value of the enormous quantities of bone-black annually used in refining sugar, glucose, mineral and other oils, etc., lies in its power to withdraw from solutions the contained organic coloring matters. After the liquid under treatment has run for some time over the bone-black, the absorption of coloring-matters by the latter is seen to diminish, and when this has proceeded to a certain point the supply is cut off, and the bone-black subsequently washed with water, naphtha, or other appropriate solvent, to wash out, as far as possible, the coloring-matters, etc., which have been absorbed by the bone-black. In spite of the most careful washing, however, some carbonaceous matter persistently clings to the char, to remove which the bone-black is heated in closed iron pipes or retorts in kilns, without the access of air. A destructive distillation of the carbonaceous matters results, driving out a large proportion of their substance in gaseous form, but still leaving a small quantity of their carbon deposited in the pores of the grains of bone-black. This accumulation of carbon is quite slow, and the char may be used about a hundred times in refining high-grade sugars before its pores become so thoroughly choked as to destroy its usefulness. The deterioration is more rapid for low-grade sugars, and in refining petroleum the deterioration is so excessive that a dozen treatments will often exhaust the char. Thus the sugar refiner finds his char about exhausted at the end of

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the year, and the oil refiner much sooner. Other minor changes take place in the char, of course, but none which can compare in destructiveness to this accumulation of carbon. When it is remembered that about three tons of bone-black are needed in a sugar refinery to each ton of sugar represented in the daily melt, and that while new bone-black costs upward of $40.00 a ton the discarded char brings only about one-third of that price, it will be appreciated what a heavy annual investment the purchase of new bone-black entails.

Some unsuccessful attempts to obviate this difficulty had been made by others, but the distinction of overcoming it belongs to Mr. Moriz Weinrich, who is already world renowned as the inventor of the steam washing centrifugal machine which bears his name. He has recently invented and patented processes and apparatus for radically improving the quality of old bone-black. One process consists of the complete removal of carbon from the bone-black and the artificial introduction of fresh carbon in smaller quantity. The other consists of a uniform partial removal of carbon when that element is excessive. The first is applicable to exhausted char, such as sugar refineries and oil refineries discard. The second is preferable for removing small percentages of carbon from bone-black which has begun to deteriorate through the choking of its pores with carbon, but which has not reached the limit of usefulness. In the first case all of the carbon is burned out by passing the bone-black in a small continuous stream through the inventor's apparatus, a nearly horizontal cylinder of sheet iron, which is heated to a dull red and revolved constantly. The char enters the drum through a central orifice in the head, closing one end, which is slightly higher than the other, and leaves the drum through peripheral openings in the head of the lower end. Within the drum longitudinal projecting ribs serve to expose the bone-black more completely to the hot air in the drum. The air enters at the openings in the lower end of the drum and either wholly or partially oxidizes the carbon in the bone-black; that depending upon the heat of the drum, the volume of air, the amount of bone-black fed into the drum, the speed of turning, etc.

In case the carbon is all removed the mineral frame-work

remains intact with its pores opened up. This bone-black can then be treated with a solution of glue or molasses, or other carbonaceous matter, to thoroughly impregnate it. Then the whole can be rendered thoroughly dry and submitted to destructive distillation in closed retorts without the access of air. The organic matter is hereby charred in the very pores of the grains of bone, and the carbon thus deposited seems to be exactly similar to that originally present. After the above recarbonization the grains must be washed with hot water to remove soluble substances; and then the char is ready for use.

In the case of partial decarbonization only one operation, that of passing through the drum, is necessary, where a high carbon char can be reduced to a low carbon char and the process regulated to remove any percentage required.

Washed char, fresh from the filters and containing those organic matters which are usually destroyed by destructive distillation in retorts or kilns, can be thoroughly cleansed by passing it through this apparatus at a heat below redness, which indicates the possibility of this method's replacing the present purification or revivification in kilns.

These methods have been investigated and tested by the author, both in the laboratory and on a working scale, in their relations to sugar refining, with eminently satisfactory results, as shown below. Some unfavorable results have, at times, appeared, but they have been due to removable causes, or have been so slight as to be negligible in consideration of the great advantages attained.

LABORATORY TESTS ON TOTAL DECARBONIZATION, ETC.

A quantity of old bone-black, discarded from a sugar refinery, and containing in the neighborhood of twenty per cent. of carbon, was heated in the open air until it was burned white. Sufficient low-grade sugar syrup, for its dry substance to be equal to about fifteen per cent. of the weight of the decarbonized char, was diluted with hot water, thoroughly mixed with the burned bone, evaporated to dryness, and the mixture then put into an iron tube, closed at one end, and having only a small vent in the cap at the other end, and heated to a dull red until all the gas was given off. This carbonized bone was then cooled

and washed with water, to remove all soluble matter, and dried. It now resembled new char in appearance, but contained only about five per cent. carbon. Three hundred cc. of this char were put into a liter bottle with 350 cc. of a solution of molasses sugar, 33° Bé. and exponent = 89.2, and heated one and a half hours in a water-bath at 175° F., with frequent agitations. New char was washed similarly and dried, and 300 cc. subjected to the same treatment. The solutions were then filtered off, and while both had been greatly lightened in color, that from the recarbonized char was considerably lighter than that from the new char. The exponent of the former was 93.0; that of the latter 92.4. The char samples were carefully washed and heated in closed tubes, as before, to remove the impurities, and again treated as before. These two samples were submitted to nine successive treatments with very dark sugar solutions, the object being to ascertain whether the artificially carbonized char would stand use as well as ordinary char. It was also found that while both samples deteriorated greatly, owing to the large amount of work which had been put upon them, the treated char was relatively as much better than the other sample at the end, as it had been at the beginning, so far as color was concerned. The new char had increased the exponent 0.17 per cent. more than the treated char, in the average of the nine tests, but while the new char had removed 66.6 per cent. of the color from the average solution the recarbonized char had removed 83.3 per cent.

FACTORY TESTS ON A WORKING SCALE.

A decarbonizing apparatus was built, consisting of a cylindrical drum of three-sixteenth inch wrought iron, nine and a half feet long by thirty inches diameter, with a central longitudinal shaft by which it is turned. The drum has a slight inclination from the horizontal and is provided with internal longitudinal ribs to raise the char a little way on the ascending side as the drum revolves. The whole is enclosed by brickwork and heated by a fire built beneath its lower end. By means of this, either a total or a partial decarbonization of char can be effected, and the amount to be burned off can be regulated to a nicety by proper adjustment.

Bone-black that had been in constant use nearly a year and containing twelve per cent. of carbon was reduced to nine per cent. of carbon and tested in the laboratory against the untreated char by the above-mentioned filtration process. The original solution used had a color = 200 on an arbitrary scale. The filtrate from the untreated char had a color = 80; that from the treated char had a color = 27.

In another test the original solution had a color of 240.

Filtrate from untreated char.....	110
" " treated char.....	20
" " over-treated char (some white grains)..	26

The same samples of char, after draining, were treated again with a slightly less amount of sugar solution.

Filtrate from untreated char,	color = 120
" " treated char,	" = 40
" " over-treated char,	" = 50

In the two treatments the untreated char removed 52.5 per cent. of the color, the treated char 87.9 per cent., and the over-treated char 84.5 per cent.

It was thought that these tests extending over one and a half or two hours might show a greater difference between the samples than tests extending over a longer period, and so the following experiment was made. Three hundred cc. of each char were heated at 175°F., with 600 cc. Muscovado sugar solution at 27° Bé. giving the following results:

Original solution had a color = 210

	One and a half hours.	Six hours.
Filtrate from house char.....	50	12
" " new char.....	40	10
" " treated char.....	20	7

showing that the treated char held its own very satisfactorily.

Further, a series of six consecutive treatments of new char, char several months in use, and the same after partial decarbonization was made. Three hundred cc. of each black were heated at 175° F. with 600 cc. Muscovado solution of 27° Bé. for ten hours, being shaken every fifteen minutes. The char was thoroughly washed, and heated in nearly closed tubes after each absorption test. The average color of the liquor going on was 152.5; that coming off was, house char, 22.8; new char, 16.4; treated char,

16.7. The treated char, although a trifle below the new char in the final average, actually deteriorated less during the tests than either of the others, and thus showed a relative improvement at the end of the experiment.

Many tests have been made on the working scale which have demonstrated the superiority of the decarbonized char over old char, and its equality in many respects to new char.

In the first of these tests a filter of house char containing 12.32 per cent. carbon, and another of decarbonized char containing 10.04 of carbon, had equal quantities of the same liquor run over them for a prolonged period, forty-nine and a fourth hours. The average liquor from the house char had a color of 25, while that from the treated char had an average color of only 15; and it was very striking that the difference in color increased as the test proceeded, the latter part of the liquor from the untreated char averaging 50, while the corresponding portion from the treated char averaged only 25. The house char withdrew 79.88 per cent. of the color present, while the treated char withdrew 87.69 per cent.

In another set of filtrations on the working scale, in a sugar refinery, a raw sugar solution, color 120 and 27.7° Bé., and exponent 90.09, was put, in the regular course of running, through filters of char respectively several months old, new, and decarbonized. The average color of that from the old char was 23; from new char, 19; from decarbonized char 18. The exponents scarcely varied, being 92.17, 92.37, and 92.09, respectively.

These are a few of a great many tests both in the laboratory and in the factory made upon char which had been partially decarbonized in a small working model which could not be controlled with the desired nicety. While the average per cent. of carbon in the decarbonized char was 10.04 per cent., or 2.28 per cent. less than in that from which it was prepared, there was a good deal of it which through different causes still contained more than eleven per cent. of carbon, and considerable which had been so over-heated as to be rendered weak as a decolorizer. These two extremes, while giving a favorable-looking average per cent. of carbon, both deteriorate the char for the purposes in hand.

Some improvement having been made in the operation of the decarbonizing drum, which, however, is still far inferior to what the inventor's design calls for, it has been possible to turn out a much more uniform product. The carbon can be reduced to any desired point and kept to within half a per cent. of the requisite figure. Having thus prepared another large quantity of char, sufficient for factory tests, another experiment was made. The carbon this time was reduced from 13.03 per cent. to 10.22 per cent., and two filters filled with these grades were run against each other. The liquor entering had a color of 110. The average of that coming from the untreated char was ten, while that coming from the treated char, all the conditions being carefully kept precisely similar, was only five. From the old char the liquor ran water-white for less than an hour; from the decarbonized char it ran water-white for more than five hours; and at the end of the run the liquor from this filter was only about as dark as that at the middle of the run from the filter of ordinary char.

Now, as to the changes in the bone-black itself: after a partial decarbonization, microscopic examination shows the decarbonization to be uniform throughout the grain. Two analyses made to illustrate the chemical changes may be quoted:

	Before decarbonization.	After decarbonization.
Carbon	12.32	8.90
Calcium carbonate	3.32	3.26
Iron	0.32	0.21
Calcium sulphate	0.904	0.877
Calcium sulphide	0.628	0.494

The most noticeable and, in fact, the most desirable changes are the reduction of carbon, with a corresponding opening of the pores and increase in absorbing power; and the reduction of calcium sulphide, which is very important for sugar refineries, in view of the deleterious action this latter substance exercises upon the sugar.

Numerous experiments showed that the calcium carbonate is not decomposed by the mild heat which suffices for oxidizing the carbon, and the slight decrease indicated above is doubtless due to variations in samples or error of analysis.

The friction of the grains of bone-black against each other in

the drum is so slight that very little dust is formed. Samples taken to represent as nearly as possible the same char before and after treatment showed per cents. of dust as follows:

	Before treatment.	After treatment.
Finer than thirty mesh....	12.56	12.64
" " fifty "	0.96	2.20

The bone-black becomes specifically lighter in proportion to the carbon lost, but this does not show in the determinations of specific gravity, probably because of the grains packing more closely after treatment. This indicates a wearing off of some sharp corners of the grains. A quantity of bone-black which, before treatment, had a sp. gr. = 1.0624, and lost 2.81 per cent. of carbon during treatment, had a sp. gr. = 1.0636 afterward.

As might be expected, the process of opening the choked pores renders the bone-black slightly more friable, as shown by the fact that a sample which, before treatment, gave 1.76 per cent. of dust, by the method described by the author in a previous paper (This JOURNAL, January, 1895), gave 2.84 per cent. after reatment. This, however, is scarcely more than is given by some new bone-blacks.

The great advantages of these inventions, then, are quite apparent. The refiner of oil, sugar, or glucose, who uses large quantities of bone-black need not discard it at a great loss after its pores are choked with carbon and its decolorizing power lost; but he can, by a very simple and inexpensive process, bring it back to its original decolorizing power, when it will last nearly, if not quite, as long as before. But by far the greater advantage is the possibility of preventing its ever getting into bad condition, by submitting it to the decarbonizing process while yet the carbon is only slightly above the normal for new char, and thus keeping it always at its maximum efficiency.

By a careful use of this apparatus it is possible to burn off the organic impurities persisting in bone-black after washing, instead of charing them as in the ordinary method of revivifying, in kilns with the exclusion of air; and it is not at all impossible that the apparatus will, in the near future, supersede the present kilns used in all factories employing large quantities of bone-black.

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