Origin, Properties and Uses of Activated Carbon

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F THE elements that make up matter, carbon is one of the most common, ranging in character from the costly diamond to coal worth but one to two dollars per ton at the mine. Its uses in one form or another are manifold. Richter's Lexicon, as far back as 1910, listed 170,000 different carbon compounds. However, the present purpose is to refer to only those forms of carbon known to possess purifying properties. These include wood charcoal, bone charcoal, activated carbons. The first two are derived from the dry distillation of wood and animal bones respectively. The latter is produced by means of patented processes from a variety of raw materials, embracing wood, sawdust, peat, rice hulls, corn husks, lignite, molasses, coconut shells, fruit kernels, waste liquors, etc.

As far back as the early Fifteenth Century, it was discovered that wood charcoal possessed some power of removing coloring matter from solutions, but it was not until the close of the Eighteenth Century that this property was put to practical use. The use of wood charcoal in medicinal preparations for man and beast is still practiced. It has served effectively as an adsorbent of sick room odors and during the pioneer days of this country, it was used as a purifier of stagnant water in cisterns and water in wells that had become fouled. The old gold prospectors in Australia threw the wood ashes from their fires into stagnant water as a primitive means of purifying.

Research, following the use of wood charcoal as a purifying medium, disclosed that carbon of animal origin was superior in this respect, resulting in the manufacture of bone charcoal from the bones of animals—a product low in actual carbon content (10%), spread over a porous structure composed of tricalcium and related phosphates. In the middle of the last century, bone charcoal was introduced into the refining of sugar and is still one of the standard processes. The product now known as activated carbon is currently described as a form of carbon possessing adsorptive properties, giving it power to attract and retain to itself impurities from any liquid with which it is brought into contact. Thus, you will note a simple physical action—and not a chemical reaction—is what takes place. One can hardly imagine a simpler process of purification. Is it strange, therefore, that it is fast replacing the old style purification methods depending upon chemical reactions which, instead of removing the impurity, change its status only, leaving one never sure it won't revert under certain conditions.

A CTIVATED carbon is supplied in an acid, alkaline or neutral condition and in the form we know it today, originated in Europe about thirty years ago, where it was manufactured on a small scale, utilized mostly in the purification of drug and pharmaceutical products, and later applied to the purification of beet sugar. It was not then referred to as such, but offered under various brand names. As a trade term, activated carbon was first applied during the war, following its development as a protective means against poison gas Again, the remarkable adsorptive attacks. properties of a carbon made "active" were recognized and its use in gas masks saved countless lives.

Up to 1912, small quantities of the highpowered adsorbing activated carbon was being imported into this country from Europe, but the use here was restricted on account of the very high cost (as much as \$1.00 per lb.) mostly for use in purifying high-priced drug and pharmaceutical products. About this time, it was introduced to the producers of raw cane sugar in Louisiana and a number of the southern planters installed a refinery process at their raw sugar mills, representing a revolutionary idea in sugar refinery practice.

Broadly, the activation processes normally involve calcination and carbonizing under controlled conditions as to atmosphere, tempera-

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ture, and in certain cases carrying on the calcination process in the presence of an inorganic compound to serve as a spacing medium; also, the use of steam, CO_2 and other gasses, all with the object of securing porosity which is generally considered coincidental with adsorption efficiency. Activated carbons are divided into two classes, functioning more or less distinctly-one, in the removal of color and odor existing as impurities in liquids; the other used as an adsorbing medium to collect, recover and purify gases. The gas-adsorbing carbons originated during the great war, of which mention has already been made. They served effectively for the adsorption and elimination of toxic gases, for which no chemical protection exists. In peace times, this same type of activated carbon is used successfully in the recovery of valuable vapors of volatile liquids, the extraction of casinghead gasoline from natural gas and as a purifier of fermentation gases employed in carbonated beverages. It is also used in gas masks that serve as safety appliances for fighting fire, coal mining, etc.

For gas purposes, a dense or compact form of carbon is preferred because of its greater capacity to adsorb the largest volume of gas in the least volume of carbon; hence the use of carbonized coconut shells as one of the preferred raw materials. Fruit pits serve equally as well. Perhaps some of you remember back in 1917 and 1918, the barrels in front of the movie houses in which you were asked to drop your old peach pits. These same peach pits, charred and activated, surely "did their bit." I believe it is now well recognized-and certainly it has been our experience-that the gasadsorbing carbons do not serve as good decolorizers and it is the exception for the decolorizing type of carbon to be effective as a gasadsorbing medium.

REMINISCENT of the early days of man-ufacturing development, we were naturally anxious to arrive at some standard method of evaluation, for the purpose of controlling and maintaining quality standards. There existed no authority, either in person or reference book, to consult and we were without compass to guide our course in this respect. Finally, we resorted to what our laboratory termed the K. V. Test, which meant that we took a petroleum base oil to which was added a standard red dye - Soudan Red III, in a carefully measured quantity, to furnish a master color solution. This, we made our indicator for color removal. It worked very well for a while, particularly on the vegetable oils; the increased decolorizing efficiency secured by improving the activated process reflecting itself on this K. V. scale. Then, we tried applying it to glycerine and ran into our first experience of the selectivity of these carbons — a well recognized principle today. With the development of our product for sugar refining, we devised a method of evaluation, utilizing a molasses solution, which acts as a correct barometer for many purposes, but does not give the complete answer though it still remains one of our standard methods of evaluation. Methylene blue and caramel are other mediums but we have reached the conclusion, that due to the distinct selectivity of activated carbons, there can be no common yardstick with which to measure decolorizing quality. To a great extent, one must function like a custom tailor and fit the product to the individual needs of the customer, As an example, take your cottonseed oil, which may be considered a pretty staple product. We had cases where samples of this oil, taken from different localities, have each required a different quality of carbon. Carbons evaluated upon one type of product seldom show any parallelism when tested on a different type of product. In many cases, other materials than coloring matter take part in the equilibrium reaction between carbon and coloring matter. In still other instances, the pH of the carbon has a great deal to do with its decolorizing power and an adjustment in this respect is necessary to give the best results. Adding to the carbons some percentage of other adsorbing or decolorizing mediums, such as bleaching clay, often has given better results in the combination than has been obtained with either clay or carbon alone. You are already familiar with this phenomena by the practice of using fullers' earth with the carbon, which we recognize must be attractive because at its low cost, it represents good decolorizing value; the carbon functioning more to give the oil the desired quality edge and thus the maximum market value.

I have already mentioned that you technical men representing an industry, itself created by research and now one of the largest and most progressive industries in the country, were the first to recognize the merits of activated carbon: thus are more conversant with it than anyone else and consequently its application to oils and fats is familiar to you. But, it may not be amiss to summarize the advantages of activated carbon to vegetable oil manufacture as follows:

(1) Removes colloidal impurities from crude oils of all kinds, which reduces refining losses by removal of bodies that tend to emulsify free oil into soap stock. (2) Possesses strong power of red color removal.

(3) Stabilizes oils (a) keeping free fatty acids to a minimum throughout processing, (b) keeping color and odor from reverting after processing, particularly in process of deodorizing completely.

(4) Removes "bloom" in case of mineral oil or other such contamination.

In closing this summary, I do not think it is out of place to mention, that while most, if not all, of the activated carbons are offered as both decolorizing mediums but few show any marked deodorizing action. As a deodorizer, certain carbons are as definitely powerful as they are decolorizers—not an unimportant factor when considered in connection with the refining of high grade edible oils. This contention is well established in the dry cleaning industry where carbon is used in the recovery of the naptha or gasoline, fouled with dirt, grease, etc., etc. Another recent example is fruit juice, possessing objectionable green color held very stubbornly in the liquid.

The manufacture and development of activated carbon must be accepted as a very definite contribution to the industrial manufacturing art, the actual extent of which cannot yet be estimated. As a modern purifier, it has expanded tremendously, horizontally in the variety of uses and perpendicularly as to the volume of consumption. While it can not truly be said that activated carbon has yet met all the demands made upon it; since its inception vast strides have been made in the elevation of its power and effectiveness. Relatively, it is still an infant industry; and as the demands made upon it are advanced and the need for it arises in still other fields, one can safely venture to predict, qualities will be made available to satisfy the need.

A BRIEF survey of the progress of use, so far, includes your own industry in which you have the responsibility of furnishing quality standards to comply with the pure food laws. Other products purified with activated carbon include: refined cane, beet and corn sugars; glucose, maple, sorghum and canning syrups; fruit juices, pectin, gelatine, glycerine, vinegar, phosphoric, citric, lactic and tartaric acids; inorganic chemicals, drugs, pharmaceuticals, solvents, milk sugar, wines, iodine and bromine recovery, dry cleaners solvent and most recently drinking water.

So much of interest has developed in the water field during the past year, that I feel sure you will not object to my dilating a little on the subject. The presence of bad tastes and odors has been giving water works operators trouble and worry for many years. Taste and odor conditions during the drought last year were just terrible and demanded a remedy. Probably, you know that most water for drinking purposes is treated with chlorine to make it safe in respect to basteria. Probably some of you have had occasion to, or must drink this chlorine-treated water. The worse the condition of the water, the more chlorine must be added which usually means pre-chlorination, post-chlorination or super-chlorination. The water people must play safe under control of the State Departments of Health. To any one who has had to drink water with the chlorine taste, I don't have to ask how he feels about this safe "water." The chlorine taste is bad enough but when you get chlorophenols, that is the proverbial "last straw."

The first attention paid to activated carbon in the municipal water field was in granular form, but this involved radical changes in water works' practice, as well as a very heavy capital outlay. Powdered carbon was first tried on a regular plant scale at Hackensack, late in 1929, utilizing the plant facilities as they existed, including a dry feed machine, already in use for chemicals. Organized introduction was only undertaken during this year and its reception has been remarkable. I can do no better than to quote from a recent paper, written and read by Mr. F. H. Waring, Chief Engineer of the Ohio Department of Health, before the Central States Water Works Association at Cincinnati a few weeks ago:

"Summarizing the experiences with the use of activated carbon in the powdered form, it appears that a very valuable adjunct to water purification is now available economically for successfully re-moving practically all varieties of disagreeable tastes and odors that occur intermittently in most water supplies. A consideration of the grief occasioned to water works officials when such tastes and odors have occurred in the past will lead most of us to believe that the added cost over relatively short intervals of time for the addition of activated carbon in powdered form, \$1.00 to \$2.00 per mil. gals., is well worth the money spent. And if the consumer were consulted the fractional cost extra for the treatment would be demanded once the results were evident. From a public health viewpoint, the writer is firmly of the opinion that sev-eral times the cost shown would be warranted to prevent the lay public from losing confidence in the public water supply as a result of unpalatable drinking water. The public confidence represented by a safe and palatable drinking water must be preserved.'

Already there are definite indications that carbon will find a place in the improvement of sewage disposal.

Treatment of water reminds me of the S.S. "Leviathan." At the beginning of the (Turn to Page 453)

Fats & Oils As Food

(From Page 446)

is large enough to produce pink discoloration provided the fat compound contains the colorless chromogen.

Discolorations ranging from greenish-blue to purple-blue have been observed in solid animal and vegetable fats. The microbiological process involved in producing the pigments is as follows: Certain yellow-producing cocci and some races of yellow-forming bacilli grow on solid fats at temperatures ranging from 39° F. to 99° F. The yellow pigment formed by these bacteria diffuses slowly into the fat. When the fat becomes rancid and peroxides appear, the pigment assumes a greenish color which in a few days deepens into blue. The original yellow pigment appears to be an oxidationreduction indicator and can be oxidized with the usual reagents to a greenish-blue color and reduced back to the original yellowish pigment with reducing agents. Bacterial oxidases and peroxides will effect identical changes in the pigment.

Certain mineral oils such as machine oils can support the growth of oidia and other fungi provided moisture is present. These growths are often a nuisance in constant temperature oil baths. Bacteria may be found in machine oils but never grow well in this medium. Streptococci, staphylococci and B. pyocyaneus found contaminating machine cutting oils may give rise to skin infections if the oils are not treated with a disinfectant. Oils and fats exert a weak antimicrobic action and it is a common opinion amongst bacteriologists that certain oils are good preservatives. Hall and van Meter¹¹ observed that the preservation of peanut butter, for example, is due to the germicidal action of the peanut oil present. They did state, however, that they believed the organism died out because of the lack of available food.

Söhngen found a number of species of bacteria capable of oxidizing petroleum, paraffin oil and other hydrocarbons.¹² In garden soils, for instance, the number of paraffin oxidizing bacteria may reach 200,000 per gram of soil. Not a few species of bacteria show the power to elaborate lipase, likewise numerous species of molds, oidia, torulae and yeast hydrolyze and oxilize fats to a limited extent. Fortunately for the industry, only a few strict lipophilic microörganisms are present in nature.

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Activated Carbon

(From Page 443)

year, they had been having a great deal of trouble. The condensate from the steam seals of the turbines had to be thrown overboard because of the oil it had adsorbed. This fresh water had to be bought in port, and it was thought advisable to make some use of it. Passing of the condensate thru columns of granular carbon removed the oil and made the water fit for boiler feed, without fear of "priming" or lost efficiency.

Circulating Rendering

(From Page 436)

From the standpoint of the physical condition of the material and the problems involved in handling, edible materials are more easily rendered by this process than the inedible. Several tests have been made on edible materials with satisfactory results.

With the present experience there is no other possible conclusion than that the Circulating Rendering Process is universally applicable for rendering on a large scale. Its use will result in improved products and considerable simplification and economy in operation.

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¹ It was thought at one time that fine emulsions of oil passed through the mucosa of the intestine unchanged. The newer knowledge is presented by W. R. Bloor-J. Biol. Chem. 15, 105, 1913; 16, 517, 1914; 25, 577, 1916.