Purification with

ACTIVATED CARBON:

Industrial
Commercial
Environmental

by

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Specialist in Activated Carbon
Research, Manufacture, Marketing
since 1915

Developed original process to manufacture activated carbon in America.

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PREFACE TO THE THIRD EDITION

Much of the text has been re-written to incorporate major changes that have developed during the past decade. The title has been altered to capture the attention of those entering fields in which the purification properties of activated carbon could be useful.

Activated carbon enters many diverse applications, and the human life span is too brief to gain first hand knowledge of all facets. Much information can be borrowed from the scientific literature, and some workers are in positions to open lines of communication with authorities in related fields. Through those avenues, much has been received to aid in the preparation of this text. Among the many individuals, who have contributed varied forms of aid, are the following:

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ABRIDGED PREFACE TO JAPANESE EDITION OF ACTIVATED CARBON.

Although technical writing is a solitary and monetarily unrewarding task, there are compensations, chief of which are the enriching personal contacts. During the writing of *ACTIVATED CARBON*, I had the priviledge of discussing many aspects with numerous authorities.

Following publication, I made many new friends as a result of a mutual interest in activated carbon. A memorable instance occurred in 1965 when I received a most friendly letter from Takashi Oda of Takeda Chemical Industries in which he expressed interest in preparing a Japanese translation of *ACTIVATED CARBON*. This I deemed a high honor and I transmitted the message to the Chemical Publishing Company of New York, N.Y. who are the copyright owners. An agreement was reached with the Kyoritsu Shuppan Company of Japan for the publication of a Japanese translation.

The translation has been made by Yoshitomo Eguchi. During a visit to the United States, he together with Yujiro Hara came to my home to discuss the many varied aspects of activated carbon. It was a delightful and memorable experience, and I will always treasure a fond memory of those two gentlemen who so truly represent the courteous and friendly people of Japan.

PREFACE TO SECOND EDITION

During the decade since the publication of the first edition of this text, entitled *Active Carbon,* new vistas have unfolded for the industrial user of activated carbon. There has been a growing awareness of the many diverse forms of carbon usefulness; new processing techniques have been developed; and granular decolorizing carbons are now available commercially.

Such forward steps have increased the spheres of activity in the industrial use of activated carbon. They often introduce problems as to the right path to follow, however, and in many ventures the potential user is denied the guidance that could be available. To explain, let us review the earlier history of adsorptive carbon in industry. We find that markets were first established in processes already using adsorbents, such as bone char and fullers earth, for the purification of sugar, fats, glycerol, etc. Within those processes there are but few trade secrets, and the success of the operation depends mainly on efficient methods of manufacture and marketing. Consequently the users welcomed any and all aid they could obtain from suppliers of carbon. In general that attitude still holds in established applications and through such cooperation future growth can be assured in those markets.

Much growth, however, also can develop through participation in new products and in new processes. Unfortunately the opportunities for the supplier to contribute know-how in such ventures are frequently restricted because of the secrecy that so often surrounds the development. The reason for secrecy is understandable: Research and development costs are high, and these costs must be recouped in the relatively brief interval between the date a new product is placed on the market and the time for competition to catch up. Understandably, profit-minded industrialists, aware of ubiquitous competition, are unwilling to make

premature disclosures even to those that could provide assistance.

An unfortunate consequence of this situation is that in many ventures that could become more efficient through the use of activated carbon, it may not be used; or it may be used ineffectively because of lack of know-how. In such situations a suitable written text can be useful because it asks no questions and carries away no data. This potential has guided the preparation of this revision. No attempt is made to furnish a definitive treatise; instead, the text is an introduction to basic principles and practices that should be considered in the industrial use of activated carbon. To that end the organization of subject matter has been altered and additional material is included.

Much of the added material is drawn from experiences during nearly fifty years' work with activated carbon. In 1915, I started with the West Virginia Pulp and Paper Company in its endeavor to pioneer the development of decolorizing carbons in this country. That endeavor culminated in the manufacture of Filtchar, the first commercial decolorizing carbon produced in America. From then till 1958, I participated in the research, manufacture, and marketing of other activated carbons including Nuchar and Suchar. On reaching retirement, I engaged in free-lance consulting. I am now associated with Barnebey-Cheney, a producer of activated carbon. I am also associated with the AMERICAN SOCIETY FOR TESTING AND MATERIALS in a research study to develop standard testing methods and nomenclature for activated carbon.

The experience of a single individual or group cannot cover an adequate understanding of all aspects of this many-sided subject. Therefore to provide a more comprehensive know-how I have sought the cooperation of others. In this I have had the assistance of sales, service, and research groups who have read sections of the manuscript, and supplied many valued suggestions. For making much of this help available, I am especially indebted to the following:

H. E. Pennington and H. B. Allport, of National Carbon Company; Jonathan C. Cooper, of Pittsburgh Chemical Company; R. W. Behrens, of Atlas Chemical Industries Inc;. Joseph M. Wafer, of West Virginia Pulp and Paper Company; H. L. Barnebey, of Barnebey-Cheney; W. C. Bokhoven and Chr. van der Meijden, of N.V. Norit-Vereeniging Verkoop Centrale.

I am also grateful to many who have contributed much in varied ways: Some supplied information needed for presenting specialized topics; some assisted in the preparation and editing of the manuscript; some drew attention to important items that otherwise would have been overlooked; still others corrected errors in the presentation. The information has been gathered for a number of years and limitations of space and memory preclude naming all who contributed. A limited list includes:

Ted Barnebey, J. D. Clendenin, Joseph E. Drudy, Marjorie Halstrick, T. J. Hassler, W. F. Heneghan, Donald K. Luke, Jr., F. M. Middleton, John J. Schanz, Jr., F. R. Schwartz, G. H. Scheffler, Evan A. Sigworth, J. H. Steen, Philip L. Walker, Jr., and Frank M. Williams.

Permission to reprint tables and figures has been acknowledged with the respective items. Some tables and figures for which permission was requested and granted have not been used because of subsequent changes in the manuscript.

I have made extensive use of the Deitz *Bibliography of Solid Adsorbents.* As it is in the form of a collection of abstracts, this publication offers the reader a better view of the content of each article than does a bare reference to the original source. Similar use has been made of *Chemical Abstracts.*

A word of explanation is in order for the change in title. The designation *Active Carbon,* used in the earlier book, is favored in a number of scientific circles, whereas most industrial workers prefer the term *Activated Carbon.* Inasmuch as this text is focused primarily on industrial aspects, it seems fitting to call this work *Activated Carbon.*

The preface to the first edition is included to establish continuity, and also to give recognition to the many persons who assisted in the preparation of the original text.

Finally, I am happy to express my perennial gratitude to my wife, Clara—my partner in all undertakings.

JOHN W. HASSLER

June, 1963.

PREFACE TO FIRST EDITION

This text has been prepared for operators and research workers in industry. I have attempted to survey principles and practices involved in the use of active carbon with the belief that an insight into the underlying features may suggest possible improvements in existing applications and also stimulate a search for new procedures.

The subject matter is grouped into three principal parts. Since many readers will be interested in only certain aspects, each part has been prepared so that it can be read independently of the others. Following an outline of the history and methods of manufacture, the next ten chapters discuss fundamental factors involved in adsorption by active carbon.

Applications are described in Chapters 13–30. A general outline is given of a number of applications, together with the specific objectives that are sought in each case. An operator will often find more helpful information from a description of how things are done in other processes than by copying what is being done elsewhere in his own field. With this in mind, some rather impractical procedures are described because they present novel approaches which could be useful in other applications.

The last four chapters cover experimental methods that have been found helpful in developing industrial applications.

Part of the information in this text has been drawn from personal experiences during thirty-five years' association with the manufacture and marketing of active carbon and this includes information received directly from other workers. To an even larger extent, the discussion is based on information in the literature. Some published data are obscure and other data are in dispute, so that it becomes the responsibility of the author to try and sift the facts. Consequently, the reader should be aware

of the fact that the text contains not only facts, but also beliefs and opinions. The inquiring reader may find statements that he will question. This is as it should be. Questions stimulate independent thinking and this is necessary to integrate new facts with older knowledge. New facts become useful when they enlarge our vision and provide a new approach to problems.

I wish to express appreciation to those authors and publishers who granted permission to reproduce data. I have been fortunate in having received suggestions, criticisms, and information from many workers who have specialized knowledge. A number of authors checked references to their work and others reviewed portions of the manuscript. Professors Elroy J. Miller, Harold J. Cassidy, and F. E. Bartell gave helpful suggestions for portions of the text dealing with fundamental aspects of adsorptive behavior. Dr. Homer Adkins reviewed the chapter on catalysis, and Dr. H. L. Riley the section on the structure of carbon. Dr. Arthur Grollman read the chapters dealing with biochemicals; solvent recovery was reviewed by Dr. A. B. Ray, and air purification by Mr. Hugh Porter. The chapters on the removal of toxic gases and that on laboratory methods of gas adsorption were reviewed by personnel of the Chemical Corps Technical Command. Mr. Robert H. Buckie reviewed the entire manuscript and assisted with a number of translations. Much information on industrial applications was furnished by my associates throughout the West Virginia Pulp and Paper Company, and I regret that space does not permit detailed mention of the many helpful individual contributions. Finally, I wish to express my deep appreciation to Mr. Joseph Wafer, for without his help and encouragement, the text would never have been started and carried through to completion.

February, 1951 JOHN W. HASSLER

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History and Market Review

"For there is nothing good or bad but thinking makes it so"
Shakespeare Hamlet

1. INTRODUCTION

Purity is a subjective concept. Salt is desirable on a breakfast egg, but not in a glass of drinking water. Pesticides benefit a growing crop, and detergents help in the laundry, but both are considered contamination when discharged into waterways.

No substance—of itself and by itself—is an impurity. Conversely, any substance can become contamination, if on entering a system, it damages desirable properties and characteristics.

Some types of contamination can be converted into acceptable forms, for example, the bleaching of an unwanted color with chlorine. But in general purification is accomplished by providing effective means of separation. The separation may be accomplished by removing the desired constituent from the system, as when pure water is distilled from salt brines; and when white sugar is crystallized from a syrup. Alternatively, it may be the contamination that is removed, as when dissolved mercury salts are precipitated and separated from the solution by filtration; or when acid gases are removed from air by contact with an alkaline solution. Some separations are accomplished through the ability of fluid molecules to adhere to the surfaces of solids—a phenomena known as *adsorption.* For practicable use, certain requirements must be met. A large surface area is essential because only a very small weight of molecules adheres to each square meter of surface.

The needed surface exists on porous solids known as *adsorbents*. Activated carbon adsorbents contain a myriad of micropores, the walls of which have surface areas that range from 400 to over 1800 square meters per gram in the various commercial brands. But more than large surface area is needed. To provide a means of separation, it is obvious that adsorption must be selective; certain species of molecules should be adsorbed in preference to others. To provide adequate purification, an adsorbent should be able to to take up and hold molecules of the substance to be removed without disturbing other constituents in the system. Moreover no single type of adsorbent surface will be appropriate for all diverse forms of contamination; therefore a variety of adsorbent surfaces should be available to handle the different needs.

It so happens that activated carbons can meet many of the diverse needs.[1,2,3] The adsorptive properties, which exist in primitive form in ordinary wood charcoal, can be developed in various forms by appropriate changes in manufacturing processes. Consequently, brands of commercial activated carbons made by dissimilar processes differ in adsorptive characteristics. Some excell for gas masks, others are superior for sugar refining, still others are best for water purification, and so on. Hence, we can quite properly consider that the term *activated carbon* comprises a family of adsorbents. That aspect extends and widens the potential utility because if one brand is tried and found wanting, possibilities remain that another brand will be suitable. Also to be considered is that the performance of carbon can often be guided into diverse channels by appropriate conditions. Consider the addition of activated carbon to a mixture of aniline and phenol in dilute aqueous solution: at *p*H 7, both will be equally adsorbed; at *p*H 10, aniline will be preferentially adsorbed; at *p*H 3, phenol will be preferentially adsorbed.

Features to be considered in the selection of carbon for use are considered in later chapters, but at this time we should mention the separate spheres of application of powdered and granular carbon. Powdered carbons are applied in a so-called *batch-contact* treatment: in this measured amounts of carbon and substance to be treated are mixed and subsequently separated by filtration. With granular carbons, the gas or liquid to be purified is passed continuously through a bed of carbon. For many years granular carbons (except bone char) were used primarily in vapor phase

systems because the early commercial brands lacked adsorptive characteristics needed for most liquid phase purifications. After World War II, new granular brands were developed having a broad spectrum of adsorptive powers, and today are in use in many liquid phase appplications. They have opened new markets that offer promise of important future growth.

The adsorptive properties of carbon were well known long before the terms *active* and *activated* had been coined. In early literature data on the adsorptive properties appear under many varied names: bone char, blood char, coconut char, and others. More recently the information appears under *decolorizing carbon* and also under individual commercial brand names.

2. HISTORY

Early history[1-2] The use of charcoal for purposes other than as a fuel and in metallurgy is very old; the use in medicine being mentioned in an Egyptian papyrus from 1550 B.C. In the time of Hippocrates wood chars were used to treat various ailments. Kehl in 1793 discussed the use of char for removal of odors from gangrenous ulcers.

The earliest date at which adsorptive powers were definitely recognized was 1773 when Scheele[1] described experiments with gases. In 1785, Lowitz[4] called attention to decolorizing effects of charcoal on solutions. A few years later, wood char was employed to purify cane sugar, and in 1808 was applied to the then infant beet-sugar industry. Figuers[1] discovery in 1811 of greater decolorizing power of bone char led to its almost immediate adoption by the sugar refiners. At first, pulverized bone char was applied on a single use and discard basis, but limited supplies made regeneration necessary. A method of regenerating granular bone char was developed and that process is still in general use in refining cane sugar.

During the 19th century, many studies were made to develop decolorizing carbons from other source materials. Bussy[5], in 1822, heated blood with potash and produced a carbon with with 20 to 50 times the decolorizing power of bone char. Blood char so produced was used for years in many laboratory studies. Hunter[6], in 1865, reported the the gas-adsorbing power of cocoa-

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