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chapter I

History and Market Review

1. INTRODUCTION

In *Chemical Abstracts*, sources of information relating to the adsorptive properties of carbon are indexed under *Carbon, Active* and *Charcoal, Active*. This text will consider primarily those carbons in which the adsorptive powers have been purposely increased by man-made operations. These are known in industrial circles as activated carbons and activated charcoals.^{1, 2, 3}

To many, the designation *charcoal* implies vegetable or animal origin, hence the designation *activated carbon* is preferred for this text because it includes all source materials—animal, vegetable, and mineral.

Hundreds of patents have been granted covering methods of activation but most of them describe different ways and means of conducting a basic procedure. In this, the source material (see Table 1:1) is carbonized under controlled conditions and the resulting carbon is usually—but not necessarily—subjected to the action of an oxidizing gas, such as steam or air at elevated temperatures.

TABLE 1 : 1
ABRIDGED LIST OF SOURCE MATERIALS FOR
ACTIVATED CARBON

- Bituminous coal
- Bones
- Coconut shells
- Lignite
- Peat
- Pecan shells
- Petroleum base residues
- Pulp mill black-ash
- Wood

The properties of the finished activated carbon are influenced by the source material used and by conditions of activation. Consequently carbons made by different procedures will be dissimilar in adsorptive properties, and can have diversity in specific utility. One type may be better for purifying sugar syrups; a different grade, superior for treatment of certain pharmaceuticals; another for vegetable oils; and so on almost *ad infinitum*. Such variations suggest that the term *activated carbon* does not define a single chemical entity but instead is a generic name for a class of substances. This aspect extends the potential utility because if one type of activated carbon is tried and found wanting there is always the possibility that another type can be found to meet the need.

Features to be considered in the selection of carbon to be used are discussed in Chapters 7, 13–15, but at this time we should call attention to the distinction between the roles of powdered and granular carbons. Powdered carbons are applied in a so-called *batch-contact* treatment; in this, measured amounts of carbon and the 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. Formerly, granular carbons were used primarily in vapor-phase adsorption, but in recent years the use has been extended to liquid-phase applications.

The adsorptive properties of carbon were well known long before the terms *active* and *activated* had been coined. In the early literature, data on the adsorptive properties appear under many varied names: *blood char*, *coconut char*, *bone char*, *lignite char*, and others. More recently references appear under *decolorizing-carbon* and also under various brand names (Table 1:2).

TABLE 1:2
BRAND NAMES OF COMMERCIAL CARBON ADSORBENTS*
(Foreign and Domestic)

Absorbit	Aktive Kohle	Bayer Carbons
Actibon	Anticarbhone	Benzorbankohle
Acticarbhone	Antichromos	Berle
Activated Carbon	Appula	Blanco
Activit	Astor	Bone Black
(also Dusarit)	Atlas	Carbac
Activon	Bachite	Carbex
Adsopur	Bactonat	Carbo Animalis
Adsorbite	Basf-Kohle	Carbo-Carbon

TABLE 1.2 (continued)

Carbo Konigsfeld	Eponit	Nigrile
Carbomel	Esbit (also Unolit)	Nobrac
Carbonaqua	Ferros De Gamus	Noir animal en pâte
Carbonit	Filtchar	Noir Diamant (also
Carbonut	Flaming	Diamantkohle
Carboraffin	Flandrac	Noir epure
Carborex	Frankonit, FK and	Noir lave en pâte
Carboserin	FC	Noir oenologique
Carbrox	Fujii	Norit
Carco	General Carbon	Nuchar
Carlisle Lumber	Girdler	Oenocarbon
Carbon	Gluconorit	Ostacol
Celchar	Glycesil	Pfeiffenberger Kohle
Celocarbon	Haller Black	Phytocarbon
Charlitt	Hamon Carbons	Pittsburgh
Chates	Hi-ac	Polycarbon
Circlene	Hiagenit	Puraire
Clacarb	Horodenka	Purit
Clarine	Humuskohle	Radit
Clarit	Hydraffin	Rennite
Claryfine	Invicta	Shirasagi
Cliffchar	Kaffeeraffin	Silica Black
Collactivit	Karbos (Carbos)	Sorboid
Colorado Fuel &	Kelpchar	Sorbonorit
Iron Carbon	Klearit	Suchar
Columbia Activated	Koblit	Sumacarb
Carbons	Kosmac	Superba
Darco	Kuri Sumi	Supersorbonkohle
Declowyte	Lignocarbon	Sutcliffe Carbon
Decolorit A	Litterale	Swastika
Denver Fir Clay	Magnechar	Sylvac
Carbon	Maximin	Synchar
Deodorite	Meade	Tilton
Deutz	Melite	Ultra-carbone
Dicalite M-23	Merke	Urbain-carbons
Dorsite	Minchar	Weschar
Dubinin Carbons	Molascarb	Westchar
Ecolite	Molaschar	Wetterau
Elorit	Morrell-carbons	Zeo Carb
Epofene	Nara Sumi	Z-Kohlen

* This list includes most of the brands of carbons that have been available to industry at some time; many of these are no longer manufactured.

2. EARLY HISTORY

The use of carbon for purposes other than as a fuel or in metallurgy is ancient; various carbons are mentioned for medicinal use in an Egyptian papyrus (1550 B.C.). In the time of Hippocrates and Pliny,

wood chars were employed for the treatment of various ailments. Kehls, in 1793, discussed the application of charcoal to gangrenous ulcers to remove bad odors.¹

The discovery of the phenomenon of adsorption, as now understood, is generally attributed to Scheele¹ who in 1773 described experiments on gases exposed to carbon. In 1777, Fontanna⁴ disclosed an experiment in which glowing charcoal was plunged under mercury and allowed to rise into an inverted tube containing a gas, whereupon much of the gas disappeared. In the realm of solutions, the earliest documented date appears to be 1785, when Lowitz⁵ observed that charcoal would decolorize many liquids. A few years later wood char was employed in a refinery to clarify cane sugar, and in 1808 the use was extended to the then infant beet sugar industry in France.

To thwart Napoleon's conquest of Europe, the British navy—which controlled the seas—placed an embargo on overseas shipments of goods and supplies. To meet the ensuing shortage of sugar, Napoleon subsidized the struggling young beet sugar industry. At first, wood char was used for decolorizing but with only partial success. About this time, Figuier¹—while preparing shoe blacking with a mixture of honey, wine, and bone char—observed that bone char had decolorizing power which he subsequently found to be superior to that of vegetable charcoal. The results were published in 1811 and led to adoption of bone char by both beet and cane sugar industries.

At first, pulverized bone char was applied on a single *use-and-discard* basis, but because supplies of bone char were limited, studies were made to regenerate the spent char for re-use. About 1828 a method for revivifying granular bone char by reburning was developed and gradually adopted. In the years since then, many improvements have been made in the process and today it is in general use in the cane sugar industry.

During the nineteenth century a number of attempts were made to prepare decolorizing carbons from other source materials. In 1822, Bussy,⁶ by heating blood with potash, produced a carbon that had from twenty to fifty times the decolorizing power of bone char. Blood char so prepared was extensively used in laboratory studies until the introduction of modern activated carbons. Bussy also enhanced the adsorptive power of other chars by various methods, some of which were rediscovered years later by others.

The great capacity of coconut char for adsorbing gases was reported by Hunter⁷ in 1865. Certain outstanding properties of coconut char have never been fully duplicated in any other char—and for some purposes coconut char is superior to all others.

Stenhouse,⁸ in 1856, prepared a decolorizing char by heating a mixture of flour, tar, and magnesium carbonate; Lee,⁹ in 1863, prepared a deodorizing carbon by the action of superheated steam and air on peat; and in 1868, Winsor and Swindells¹⁰ heated wastes from paper mills with phosphates. Some of the disclosures are similar to processes that are in current industrial use, and it is natural to inquire why they were not then developed on a commercial scale.

One answer can be found in the manufacturing problems that are involved. Although activated carbon can be prepared with relative ease on a laboratory scale, the industrial production is attended by engineering difficulties. The corrosive action of many activation conditions requires special structural materials that were not then available. Moreover, the successful industrial production of activated carbon depends on the skill of the manufacturer in controlling the environment of activation within narrow limits, and suitable instrumentation for such control is a relatively recent development.

Another factor that retarded the industrial development was the absence of an apparent need for a carbon more adsorptive than bone char. Apart from laboratory studies, we find records of only a few isolated attempts to utilize the adsorptive power of carbon in fields other than sugar refining. However, it is of interest to note certain suggested applications that years later became important markets for activated carbon. Lipscombe,¹¹ in 1862, prepared a carbon to purify potable water; Stenhouse,¹² in 1854, suggested the use of charcoal to ventilate sewers and later described the forerunner of the modern gas mask.

3. RECENT HISTORY

Inventions patented by Ostrejko¹³ in 1900 and 1901 paved the way for the development of modern commercial activated carbons. In one patent he described a basic process in which metallic chlorides were incorporated with vegetable substances and the mixture then carbonized at a suitable temperature. In another patented process, vegetable charcoal was heated at bright red heat with the simultaneous action of carbon dioxide.

The first powdered commercial carbon, Eponite, was produced in Europe in 1909, using wood as a source material and working under the Ostrejko patents.¹ Norit, an activated carbon manufactured in Holland, first appeared about 1911 and soon became widely known in the sugar industry.

The first activated carbon produced in America was developed accidentally from an endeavor to find utility for leached black-ash, a waste product in the manufacture of soda pulp.²⁶ When pulverized, black-ash resembles lamp black, and a factory was erected to process it into a pigment. Because of certain color characteristics, however, the finished pigment was not generally accepted by the paint and ink industries. Vigorous efforts to find other sales outlets were of no avail and the factory was about to be abandoned, when, quite by accident, one of the workers stumbled on the discovery that black-ash has decolorizing power. The product, now named Filtchar, was sold as a substitute for bone char and fuller's earth. Marketing difficulties soon developed because of uneven quality of the product; some batches were satisfactory, others were not. Very few tests were then available to measure decolorizing power and none were suitable for quality control of the Filtchar.

Research developed the test with Sudan III dye to measure the relative efficiency of each batch of Filtchar,¹⁴ and by selection it became possible to furnish activated carbon of satisfactory uniform quality to consumers. But the test accomplished much more for it was now possible to study factors that influenced the decolorizing power of black-ash, and within a short time carbon of improved quality was produced.

Early interest in the development of activated carbon was stimulated by a belief that a large potential market existed in the cane sugar industry. Some early studies seemed to indicate that powdered activated carbon could be applied directly to the raw cane juice and thereby eliminate the need for an intermediate stage in which raw sugar is first produced, which then must be redissolved and recrystallized. However, this hope was not realized; factory operation disclosed that the intermediate stage of raw sugar was still necessary.

Powdered activated carbon was found to be an effective substitute for bone char in established operations but required the installation of new specialized equipment. Inasmuch as the existing equipment for bone char represented a large capital investment, very few refiners were induced to make the change.

Sales opportunities were found for the purification of other products that require decolorization but the total extent of such markets fell far short of fulfilling the hopes of those that had pioneered in the development of what were then known as decolorizing carbons.

Then, in 1915, an event that shocked the world brought fame to activated carbon. World War I had become a purely defensive action with opposing armies land-locked in trenches. Seeking to break the impasse, the German command on April 22, 1915 ordered the release of chlorine from cylinders on a four-mile front near Ypres,¹⁵ and a breeze carried the yellow-green vapor over no-mans land into the Allied trenches. Against this weapon the Allied soldiers had no protection; the agonized men, choking and gasping, could only flee, leaving a breach in the line. Had the Germans conducted the attack over a wider front and followed through the breach, they might have won a decisive victory. But the German soldiers themselves had no protective armour to withstand the effect of the gas, and so could not follow through. Soon afterwards, another attack was made with similar results. The Germans then turned to a study of other methods of gas warfare and the interval gave the Allies an opportunity to provide protection in the form of gas masks containing activated carbon. Had it not been for this development, history might have followed a far different course.

Although activated carbon had been manufactured for some years, the soft powdered types were not suitable for gas masks. Consequently new materials had to be selected and new processing equipment developed. Coconut char proved to be a suitable source material because of its great potential adsorptive capacity combined with the required resistance to abrasion. The rapid development of effective methods of production constitutes a brilliant episode in the annals of industrial chemistry.

4. MARKETS^{16, 17, 21}

The publicity given to activated carbon in World War I stimulated research to extend the use of it in new fields, and the years since then have witnessed a steady growth in production. (See Tables 1:3 and 1:4).

Air Purification

The principle of the gas mask is employed to eliminate odors and noxious vapors from living and working spaces. Such use has gained

momentum in recent years with the introduction of air conditioning. The traditional method of removing odors and correcting a stale and vitiated atmosphere in living quarters is by ventilation with fresh air from outside. The admission of large quantities of outside air, however, can increase the costs of air conditioning to a prohibitive level.

TABLE 1 : 3
RANKING OF MARKETS FOR ACTIVATED CARBON*

<i>Sales Volume, Pounds</i>	<i>Sales Volume, Dollars</i>
1. Municipal Water Purification	(2)
2. Corn Sugar	(1)
3. Cane Sugar	(7)
4. Gas Adsorption	(3)
5. Dry Cleaning	(4)
5. Reclaimed Rubber	(8)
7. Pharmaceuticals	(5)
8. Fats and Oils	(6)
9. Beet Sugar	(11)
10. Plasticizers	(10)
11. Industrial Water Purification	(9)
12. Electroplating	(12)
13. Alcoholic Beverages	(13)

* From thesis by Richard H. Parry, December 1961;¹⁶ reprinted by permission of Department of Mineral Economics, Pennsylvania State University.

In many situations, therefore, it has become more general practice to recirculate much of the air and maintain the purity and freshness by passing the air continuously through a bed of granular activated carbon. In areas where smog prevails, outside air should be passed through activated carbon before being admitted to living quarters.¹⁸

Air purification can be helpful wherever groups assemble in enclosed quarters, e.g., restaurants, offices, public transportation, air raid shelters.¹⁹ In submarines, activated carbon prevents the accumulation of an odor in the air that is re-used many times.²⁰

Solvent Recovery

A market has been developed for the recovery of organic solvents used in diverse industrial operations: as processing mediums in the manufacture of plastics, explosives; and as agents to apply a product to its intended use as in painting and printing. Many such solvents are volatile and the escape of such vapors into work rooms can create hazards to health, and from fire and explosion. As the amount of

solvent thus vaporized can constitute an appreciable cost, recovery is desirable also for economic reasons. The liquid is recovered by passing air from the work rooms through beds of activated carbon, and the adsorbed vapor is subsequently removed from the carbon with steam.

TABLE 1 : 4
U.S. PRODUCTION, VALUE, AND AVERAGE UNIT
VALUE OF WATER PURIFICATION AND
DECOLORIZING GRADES OF ACTIVATED CARBON
FOR SELECTED YEARS
1935-1960*

<i>Year</i>	<i>Production</i> (short tons)	<i>Value</i> (dollars)	<i>Average Unit Value</i> (cents per pound)
1960	60,118	15,870,000 ^e	13.2 ^e
1959	58,436	15,451,000	13.2
1958	53,297	13,834,000	13.0
1957	52,757	12,953,000	12.3
1956	53,469	11,608,000	10.9
1955	48,518	10,318,000	10.6
1954	46,200	9,326,000	10.1
1953	42,388	8,555,000	10.1
1952	32,446	6,744,000	10.4
1951	41,656	7,656,000	10.1
1950	37,921	6,737,000	8.8
1949	33,558	NA	NA
1948	33,016	NA	NA
1947	36,169	4,249,000	5.9
1946	32,551	NA	NA
1945	31,289	NA	NA
1944	30,785	NA	NA
1943	29,625	NA	NA
1939	16,168	1,881,000	5.8
1937	10,655	1,444,000	6.7
1935	11,477	925,600	4.3

^e, Estimated.

NA, Data not available.

Source: U.S. Department of Commerce, *Census of Manufacturers; Facts for Industry*.

* From Thesis by Richard H. Parry, December 1961;¹⁴ reprinted by permission of Department of Mineral Economics, Pennsylvania State University.

The adsorption of vapors, with or without recovery, is essential in many diverse industries. In most instances the vapor adsorption can be accomplished in equipment of established design, which when necessary can be altered or modified for specific needs and conditions.

Although the basic features of such adsorption systems are simple, proper correlation of the component units and careful attention to details are essential to efficient operation and often to safety. Inasmuch as measures to correct vapor pollution rarely need to be concealed, there is seldom any objection on this score against placing such projects in the hands of a qualified engineering group outside, and thereby achieve a more efficient operation at a lower cost.

Liquid-Phase Applications

The interest that had been aroused by the publicity given to the use of carbon in gas masks in World War I extended to liquid-phase purification, and workers in many industries began to explore possible benefits from the use of activated carbon. Considerable enthusiasm also developed in the direction of additional facilities for manufacturing activated carbon. As a result the period following World War I was marked by intense competition. Of the hundred or more brands of commercial carbon developed during that period, only a few remain. The quest for survival led to continual advancement in the quality of activated carbon. Within a space of twelve years, the process based on black-ash went through four major changes in method of manufacture.

Intense competition led to a search by suppliers for new and greater sales outlets. Primary consideration was given to decolorization, and the term so generally used—*decolorizing carbon*—mirrors the thinking of the times. Those that used carbon for decolorization often discovered other benefits, such as improvements in other properties of the product being decolorized. It was found, too, that carbon often aided processing stations by adsorbing impurities that interfered with functions such as filtration, evaporation, and crystallization.

Suppliers recognized the need for a good descriptive name to advertise the many-sided properties of activated carbon. This resulted in slogans such as "Activated Carbon, the Modern Purifier". The name *decolorizing carbon* has survived and continues in general use, but at least it has come to mean a carbon having a broad spectrum of usefulness.

In many food industries, decolorization led to the use of carbon for the removal of unwanted flavors and odors, and this, in turn, may have planted the thought leading to the use of carbon for purifying potable water supplies. During recent decades, great strides have

been made in the disinfection of water supplies and in the elimination of tastes and odors. Although the control of tastes and odors has been a relatively recent achievement, the problem is by no means new.²² We know the identity of only a few of the multitude of substances that can and do cause taste and odor in water. Furthermore, the specific cause will vary from one supply to another, and even in any one supply the cause can change from season to season. Many means of correction had been studied—superchlorination, aeration, chloramines, ozone, permanganate—but with only limited success.^{23, 24} It had long been recognized that activated carbon would remove tastes and odors; but because of cost there was hesitation to use it on municipal supplies, particularly because a large proportion of the treated water is used for purposes in which palatability is not essential.

The meat packing industries of Chicago are credited as being the first in America to use activated carbon for water supplies. This was in 1928.²⁴ Then in 1930, the New Milford plant of the Hackensack (New Jersey) Water Company had trouble with a very disagreeable taste that resisted other means of correction. Finally Spalding²³ experimented with powdered activated carbon, and the promising results led to a plant scale test that was a complete success and furnished a fully palatable water. Spalding's success was recognized by the supervisors of other water plants, and by the end of 1930, activated carbon was being used in over 150 plants.²⁵ The figure rose to 400 plants during 1932 and passed the thousand mark by 1938.

Although activated carbon is a "natural" for water purification, the development of this application was not without many problems. That they were solved so rapidly and effectively can be credited to the cooperative spirit prevailing in an industry in which ideas and know-how are exchanged without let or hindrance.

With greater knowledge of the properties of activated carbon has come an understanding that it is often possible to guide adsorption into desired channels by providing an appropriate environment. Recognition of such ability has extended the utility of carbon and has made it practicable to reach markets not visualized in earlier years. In fact, some applications would seem to require a broader description than is encompassed by *purification*.

Some new applications are reminiscent of an earlier use. Thus, carbon was employed years ago to provide a gradual release of drugs

taken internally. Similarly, the recovery of antibiotics has a prototype in an earlier process to obtain iodine from brines. What is new is a greater understanding of the factors that are involved.

In one new development, activated carbon is employed as a reservoir to maintain vapor and solution concentrations at desired levels. Such action is based on the fact that a substance in the adsorbed state becomes less volatile and less soluble. This behavior has been utilized in applying systemic insecticides. These powerful agents are readily soluble and in strong concentrations, they can damage plant life. Consequently, the total quantity necessary for seasonal protection cannot be applied in a single application; that is, not under ordinary conditions. In a suitable mixture with carbon, however, the adsorbed insecticide is released gradually and the concentration in the environment is kept at a safe level.

It will be apparent that the foregoing application of carbon as a reservoir depends on the ability of carbon to release an adsorbed substance—a behavior known as *desorption*. In the foregoing example, a substance is adsorbed from a strong concentration and is released as a dilute solution. The application can be reversed; that is, a substance is adsorbed from a very dilute concentration and released as a much stronger concentration. An illustration is found in a process that expedited the production of penicillin when it was so critically needed during World War II. In that process, activated carbon was added to a fermented broth containing about 30 ppm penicillin. After removal from the broth, the carbon was extracted with acidified methanol which eluted the adsorbed penicillin in a relatively concentrated form.

Adsorption-desorption processes have been very successful with vapor systems. In contrast, the experiences with liquid systems have provided many disappointments, and the hopes once held for large markets remain unfulfilled. Probably research on fundamental aspects could do much to place future applications in this field on a sounder footing.

Plastic Solids

The applications described thus far are limited to gaseous or liquid systems, and some mention should be made of the use of carbon in plastic solids. Knowledge of the migration of color in plastics solids dates back to the early days of oil painting when the expense and scarcity of canvas often led artists to paint over an

earlier painting. In such cases, the colors in the original would bleed through and cause obvious damage. Similar experience is encountered with materials of today, such as light-colored linoleum, plastic vinyl tile, and white-sidewall tires.

Let us consider white-sidewall tires. These are formed by placing a layer of white rubber over a carcass of dark rubber. Under normal conditions, molecules of color in the carcass migrate and bleed through to stain the white-sidewall. This staining can be prevented by incorporating activated carbon in carcass rubber. Then the colored molecules will migrate only until they reach a particle of activated carbon, whereupon they become adsorbed and anchored.

Miscellaneous

The examples that have been discussed were selected because they serve to illustrate the many-sided nature of activated carbon. Those that have been associated with the industrial development of activated carbon recognize that many, perhaps most, specialized applications have been discovered by workers in other fields—workers that had the vision and imagination to utilize adsorption to improve products and processes that they were developing. Their endeavors have contributed much to the growth of markets for activated carbon.²⁶

Such contributions have come because of intelligent self-interest; but the net effect is equivalent to having silent partners in many and varied research and development groups who are in a favored position to create new markets for activated carbon. Often the new projects have been a joint undertaking, in which the suppliers of activated carbon furnish much of the needed know-how to expedite the progress of a new project. Some years ago, however, there appeared a proverbial "Cloud no bigger than a man's hand", namely, the secrecy that now surrounds most new projects. This often precludes opportunities for participation by outsiders, among whom are the research workers in the industry of activated carbon. The net effect is doubly unfortunate, for it not only hinders the use of existing know-how in expediting projects but it is also drying up the wells of new knowledge.

REFERENCES

1. Deitz, V. R., *Bibliography of Solid Adsorbents*, United States Cane Sugar Refiners and Bone Char Manufacturers and National Bureau of Standards, Washington, D. C., 1944: History of adsorbent carbon, p. ix ff; abstracts of reviews, histories, and general discussions, pp. 689-696.
2. Bancroft, W. D., *J. Phys. Chem.*, 24: 127, 201, 342 (1920).
3. Zerban, F. W., *Louisiana Agric. Exper. Sta. Bulletin*, 161 (1918).
4. Fontana, F., *Mem. Mat. Fis. Soc. Ital.*, 1: 679 (1777).
5. Lowitz, *Crell's Chem. Ann.*, 1: 211 (1786).
6. Bussy, A., *J. Pharm. Sci. Accessoires*, 8: 257 (1822).
7. Hunter, J., *J. Chem. Soc.*, 18: 285 (1865).
8. Stenhouse, J., British Patent 1395 (1856).
9. Lee, T. V., British Patent 528 (1863).
10. Winsor, F., and Swindells, J., British Patent 835 (1868).
11. Lipscombe, F., British Patent 2887 (1862).
12. Stenhouse, J., *Chem. News*, 3: 78 (1861); 25: 239 (1872).
13. Ostrejko, R. von, British Patents 14224 (1900); 18040 (1900); German Patent 136,792 (1901).
14. Wickenden, L., and Hassler, J. W., *Ind. Eng. Chem.*, 8: 518 (1916).
15. *Encyclopedia Britannica*, 14th Edition.
16. Parry, Richard H., *Thesis*, Pennsylvania State University, Dept. Mineral Economics, Dec. 1961. This thesis furnishes a comprehensive analysis of the markets for activated carbon in America.
17. *Chem. Eng. News*, Aug. 15, 1960; June 19, 1961.
18. Richardson, N. A., and Middleton, W. C., *ASHAE Journal*, Nov. 1958.
19. Pennington, H. E. of National Carbon Company reports that many building codes require fresh air make-up on basis of occupancy. Personal communication.
20. Ratcliff, J. D., *Readers Digest*, July 1958; *Today's Living*, June 22, 1958.
21. Schanz Jr., J. J., and Parry, R. H., *Ind. Eng. Chem.*, 54 No. 12: 24 (1962).
22. Bayliss, J. R., *Elimination of Taste and Odor in Water*, McGraw Hill Book Co., New York, 1935.
23. *Taste and Odor Control in Water Purification*, Industrial Chemical Sales Division, West Virginia Pulp and Paper Co., New York, 1947; contains 1063 classified references.
24. Hassler, W. W., *J. Am. Water Works. Assoc.*, 33: 2124 (1941).
25. Wrench, J., *Eng. Contract Record*, 50: 610 (1935).
26. Hassler, J. W., *Forest Products J.*, Vol. 8 No. 6: 25.A (1958).