# **Kynol Europa GmbH**

Tel. +49 (0) 40 - 53 00 45 - 0 Fax +49 (0) 40 - 53 00 45 - 45 mail@kynol.de · www.kynol.de



Kynol Europa GmbH · Borsteler Chaussee 55 · D-22453 Hamburg

# ACTIVATED CARBON FIBERS AND TEXTILES Properties and Applications

Joseph S. Hayes, Jr.

#### ABSTRACT

Activated carbon fibers are highly porous carbon fibers with specific surface areas of 700 to 3000 m²/g and pore volumes of 0.35 to 0.80 cm³/g or more. Fiber diameter is typically 10  $\mu m$ , while the pore structure consists almost entirely of micropores with half-widths on the order of 1 nm; therefore the dynamics of adsorption are much superior to those of conventional granulated or powdered activated carbons.

Produced from suitable precursor fibers such as novoloids, or from textile structures made from such precursors, activated carbon fibers and textiles have applications ranging from filtration and solvent recovery through electronics and even ceramics.

### CARBONIZATION - Carbon fibers

While activated carbon fibers can be obtained from several types of precursor fibers, Kynol<sup>m</sup> novoloid fibers are particularly suitable as precursors because of their high carbon content and amorphous molecular structure.

Figure 1: Novolac resin

Figure 1 shows the typical chemical structure of novolac resin, made by polymerization of phenol and formaldehyde, and containing about 78% carbon. Fiberizing such a resin and crosslinking with additional formaldehyde yields novoloid fibers, three-dimensionally crosslinked network polymers containing about 76% carbon (Figure 2). (1)

$$-CH_{2} - CH_{2} -$$

Figure 2: Novoloid fiber

Novoloid fibers are readily processed using conventional textile techniques into yarns and fabrics, and these in turn may be converted by pyrolysis under suitable conditions into carbon or activated carbon fibers and textiles. (In this paper carbon materials of low specific surface area, on the order of 1  $g/m^2$ , will be referred to simply as "carbon"; and those with specific surface areas over several hundred  $g/m^2$ , as "activated carbon".)

Let us first consider what happens to novoloid fibers when they are heated in an inert atmosphere such as nitrogen, with sufficient gas flow to sweep away the byproducts of pyrolysis. As the temperature reaches 300°C, the fibers begin to lose some of their hydroxyl (-OH) and methylol (-CH<sub>2</sub>OH) groups (Figure 3).

Figure 3: Novoloid fiber pyrolyzed in  $N_2$  at 300°C; approximately 76% carbon.

Further heating results in continued loss of non-cyclic elements including the methylene (- $\mathrm{CH_2}$ -) bridges, and then of hydrogen, with gradual coalescence into a polycyclic carbonaceous structure (Figures 4 and 5). These molecular changes are reflected in observable (macroscopic) shrinkage of about 20%.

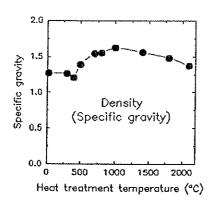
Figure 4: 400°C, 85% carbon

Figure 5: 500°C, 90% carbon

Finally, as the treatment temperature passes 700°C, a planar hexagonal carbon structure is achieved, as shown in Figure 6. However, due to the unorganized structure of the precursor these structured domains are extremely limited in extent and the material as a whole remains amorphous and noncrystalline. This amorphous structure is reflected in a comparatively low modulus of elasticity (high flexibility), and in lower density and lower electrical conductivity than those of carbon fibers based on PAN (polyacrylonitrile), for example. X-ray diffraction studies show only broad peaks, indicating very little crystallinity.

Figure 6: 700°C, 95% carbon

The density (specific gravity) at various stages of carbonization is shown in Figure 7. For comparison, the density of single graphite crystals is about 2.26, while that of high-modulus carbon fibers is typically in the range from 1.8 to 1.9. Even heating to 2000°C, while yielding high carbon purity of more than 99.8% (Figure 8), does not alter the fundamentally amorphous structure of these fibers. (2)



100 88 90 Carbon content

70 500 1000 1500 2000

Heat treatment temperature (°C)

Figure 7: Changes in density on carbonization.

Figure 8: Carbon content vs. treatment temperature.

The properties of these carbon fibers depend mainly on the treatment temperature, and are only slightly influenced by heating rate. As shown in Figure 9, at treatment temperatures over 700°C yields of approximately 55% are obtained irrespective of heating rate, so long as oxidizing gases are rigorously excluded. Figure 10 shows changes in tensile strength at heating rates of 100°C and 700°C per hour; again, ultimate temperature is clearly a more important parameter than the rate of heating.

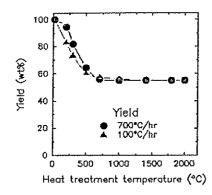


Figure 9: Carbon yield and treatment temperature at different heating rates, in N<sub>2</sub>.

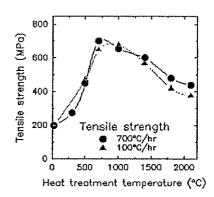


Figure 10: Changes in tensile strength during carbonization in  $N_2$ .

As Figure 9 makes clear, most of the weight loss occurs during the earlier stages of pyrolysis, in the temperature range between 300°C and 700°C. As noted above, this loss in weight is accompanied by an essentially isotropic shrinkage of about 20% (Figure 11).

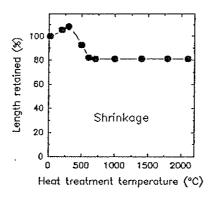


Figure 11: Shrinkage during carbonization.

# ACTIVATION - Activated carbon fibers

In the preceding we have discussed carbon fibers made by heating novoloid precursors to around 800°C in an inert atmosphere. If, however, an oxidizing gas such as oxygen,  $\rm H_2O$ , or  $\rm CO_2$  is present during heating, the fibers are not only carbonized but also "activated" through gasification of a part of the carbon and the resulting formation of a highly porous structure. In air, pore formation begins at relatively low temperatures, prior to the formation of the condensed polycyclic carbon structure; with  $\rm H_2O$  activation begins at around 700°C, and with  $\rm CO_2$ , at around 900°C, following (or simultaneous with) formation of the carbon structure described in the preceding section.  $\rm (^3)$ 

Air activation of novoloids, although economically attractive, has only recently begun to receive thorough study. Accordingly the following discussion will deal solely with materials activated by water vapor and/or carbon dioxide. In actual practice, activation is readily carried out simply by exposing the fibers or textile structures to the products of combustion of natural or liquefied petroleum gas at 900°C to 1000°C.

The extent of activation depends on the duration of exposure to the hot activating gases; as gasification continues, the pores are enlarged and the weight of the remaining material decreases. This is reflected in increasing specific surface area, the notional surface area in square meters per gram of remaining material, as measured (for instance) by the well-known "BET" method of Brunauer, Emmett, and Teller.

Figure 12 shows the relationship between specific surface area and yield of carbon; while Figure 13 illustrates the correlation between specific surface area and the total volume of pores of half-width less than 10 nm (as determined by  $\rm N_2$  adsorption at -195°C using the BET model), as well as the almost negligible volume intrusion). (3,4) pores of larger mercury (measured by It is important to note that the points of Figure 12 generally correspond to a fairly constant surface area of around 450 m<sup>2</sup> per gram of material prior to activation. This in turn implies that, once a certain initial level of carbonization and activation has been attained, further increases in specific surface area and pore volume are the result not of the creation of new surfaces or the opening of new pores, but of the gradual etching away of the remaining carbon. Higher square meters per gram means not more square meters, but fewer grams.

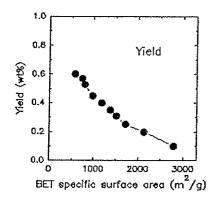


Figure 12: ACF yield and specific surface area.

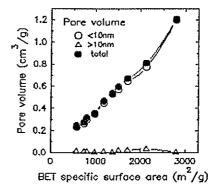
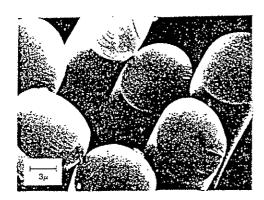


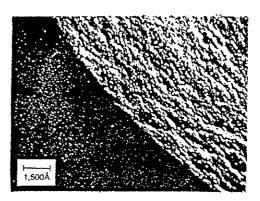
Figure 13: Pore volume and specific surface area.

Discussion of fibers with different levels of activation is facilitated by the use of nomenclature based *loosely* on the nominal (or notional) specific surface area, in hundreds of square meters per gram; thus "ACF-10" designates an activated carbon fiber with a specific surface area of approximately  $1000 \text{ m}^2/\text{g}$ .

#### PORE STRUCTURE

The electron micrographs of Figures 14 and 15 show portions of both lateral surfaces and broken ends of activated carbon fibers. The amorphous ("glassy") nature of the carbon appears to be reflected in the fact that the fibers break cleanly when broken. These fibers, made from 2 denier (15  $\mu \rm m)$  novoloid precursors, are about 10  $\mu$  in diameter. The pores themselves are too small to be detected even in the highly magnified view of Figure 15; attempts are currently being made to obtain direct evidence of pore size and configuration using scanning tunneling electron microscopy and neutron scattering techniques.





Figures 14, 15: Scanning electron micrographs of novoloid-based activated carbon fibers.

It has, however, been convincingly demonstrated by indirect evidence that the pores, or at least the pore openings, in these activated carbon fibers are slit-shaped. (5) The distribution of pore sizes, moreover, is remarkably sharp; at a given level of activation the half-widths of the great preponderance of the pores are close to a specific characteristic value, which increases with increasing activation. (For slit-shaped pores, the term "half-width" seems clearly preferable to the conventional This is clear from Figure 16, which shows cumu-"pore radius.") lative pore volume plotted against increasing pore size for fibers of two levels of activation. There is a single, sharp upswing in the curve at the characteristic half-width; and both total volume and characteristic half-width are larger for the more highly activated ACF-20.

The same information is given in Figure 17 in noncumulative form; here the sharp peaks correspond to the midpoints in the rising portions of the curves of Figure 16 -- that is, to the characteristic mean pore widths for the two levels of activation. For this figure the peaks have been normalized to the same height to facilitate comparison. Also, particularly clear examples of experimental data have been chosen for reproduction; broader peaks and those with "shoulders" are also encountered. Finally, the numerical half-width values shown are dependent on the use of a specific model for interpretation of the data, and may give an impression of exactness which is unwarranted.

Nonetheless, despite all these caveats, Figures 16 and 17 are accurate and representative in depicting the marked predominance of pores of half-widths on the order of 1 nm, with no other significant peaks encountered even as the curves are extended all the way to 10<sup>4</sup> nm -- the diameter of the fibers themselves.

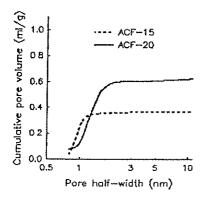


Figure 16: Cumulative pore-size distribution.

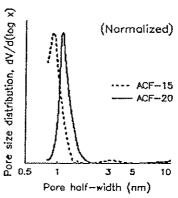


Figure 17: Pore-size distribution curves.

It is quite clear from Figures 13, 16, and 17 that the pores in these novoloid-based activated carbon fibers are essentially all micropores (pores with half-widths less than about 1.5 nm). There are virtually no macropores (over 100 nm) or transitional pores (between micro- and macro-). This is a key factor in the excellent adsorption dynamics of the fibers; since rates of adsorption and desorption are controlled by diffusion of adsorbate molecules from a gas or liquid medium into the micropores, where actual physical adsorption takes place, it is highly advantageous that these be connected to the exterior of the fibers directly, rather than through the network of intermediate and macropores which is characteristic of granular activated carbon.

Although full details of the mechanism of activation and of the resulting pore structure remain to be elucidated, certain hypotheses may be advanced. It has been noted above that activation takes place at carbonization temperatures, and that carbonization itself involves coalescence of the aromatic rings of the novoloid precursor into micro-domains with the characteristic layered hexagonal structure of graphite. Because of the unorganized structure of the precursor these domains are believed to remain strictly limited in extent, discontinuous, and imperfect, with both voids and amorphous carbon in the interstices. It is suggested that pore formation starts in these interstitial regions between the graphite-like lamellae or microcrystallites; and that once pores have opened up, pore enlargement proceeds through oxidative attack on the lamellae themselves.

Novoloid-based activated carbon fibers are thought to be completely porous. No difference between center and surface material is discernible by electron microscopy (Figure 15). Equally important, it is difficult to imagine the formation of specific surface areas and pore volumes of the observed high

magnitudes if part of the fiber remained nonporous. As a model for the fine structure, it may be best to think of a heap of sliced carrots, large and small -- or a sackful of coins -- rather than the "ribbon-network" structures suggested for highly oriented, high-strength carbon fibers made from other precursors.

The actual dimensions of the pores are on the molecular order of magnitude. On this scale, where matter is often considered in terms of "probability clouds" describing the distribution of electrons and other subatomic particles, it may well be that our commonsense notions of "surfaces" and "voids" as well-defined and hard-edged objects (or holes) no longer apply and a different geometry must be employed. Nonetheless, assuming a density of around 2 g/cm³ for the remaining carbon and applying ordinary geometrical reasoning would lead one to conclude that the pore volume of a fiber of specific surface area of 2500 g/m² must be about 2/3 of the total apparent fiber volume; that the average thickness of the carbon between pores is on the order of 0.4 nm (implying only two layers of fused graphite-like hexagons); and that average pore half-width is around 0.4 nm. (2) The first two of these conclusions are in reasonable accord with experimental observation, but the third implies values less than half those calculated using the BET model or inferred from dyestuff studies. (5)

As these apparent contradictions demonstrate, the theory and models for understanding such surfaces, and the methodology of analysis based on these models, are still fraught with arbitrariness, inconsistency, and confusion. It seems probable that the concept of surface area is itself flawed; specific pore volume (which can be measured more directly) is probably a more useful descriptor. No matter how careful the measurements and calculations, all of these numbers in the end rest on the assumptions on which the BET and other models are based. While extremely useful for comparative and predictive purposes, they are not necessarily descriptions of reality.

Table I: Typical properties of activated carbon fibers

	ACF-10	ACF-15	ACF-20	ACF-25
BET surface area, m <sup>2</sup> /g <sup>(*)</sup>	1200	1500	1750	2100
Benzene adsorption, wt%(†)	25	40	65	80
Iodine number, mg/g(§)	1300	1500	1700	1900
Pore volume, cm3/g(**)	0.35	0.50	0.65	0.80
Pore half-width, nm(††)	0.8	0.95	1.1	1.3

<sup>\*</sup> Specific surface area by  $\rm N_2$  adsorption at -195°C, BET model.

<sup>†</sup> Adsorption from gas stream saturated with benzene, 25°C.

<sup>§</sup> Adsorption of iodine from aqueous solution at 25°C.

<sup>\*\*</sup> Pore volume estimated by condensation of No and various organics.

<sup>††</sup> Consensus estimate; values relative, use with care; see text.

Having said all this, we present in Table I a rough summary of typical data for novoloid-based activated carbons at four levels of activation. The specific numerical values, particularly those for pore half-width, are dependent on the methods and models used. While useful for comparison, they should be regarded as having only relative physical significance.

## **ADSORPTION**

A more practical approach to the description and classification of activated carbons relies on their capacity for adsorption of standard substances. Figure 18 shows the capacities of the fibers of Figures 12 and 13 to adsorb iodine (from water, giving the "iodine number"); benzene (15.5 vol% in  $N_2$ ); and methylene blue (a dye often used to measure decolorization efficiency).

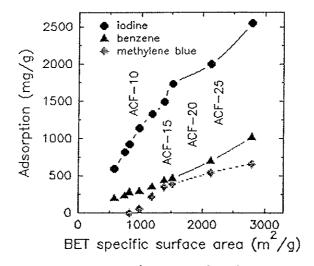


Figure 18: Adsorption of iodine, benzene, and methylene blue by ACF of different specific surface areas.

Kasaoka et al.<sup>(5)</sup> have shown that novoloid-based activated carbon fibers can act as molecular sieves, a result of the very narrow pore size distribution. This allows the separation of adsorbates by molecular size; molecules too large to enter the micropores are simply not adsorbed. These investigators also indicate that for gaseous adsorption, flat molecules (e.g., benzene) enter the pores in an orientation parallel to the slit opening; while dyes and other flat molecules adsorbed from liquids seem to orient themselves perpendicular to the pore axis.

Another interesting consequence of the narrow pore size distribution is that, at low concentrations, equilibrium adsorption of activated carbon fibers with low specific surface areas is actually higher than that of fibers with higher specific surface areas. This is illustrated in Figure 19 for n-butane in concentrations from under 100 ppmv to 100% (10<sup>6</sup> ppmv). In pure butane ACF-25 clearly shows the highest adsorption, but as con-

centration decreases, each of the lower surface area fibers takes the lead until, at concentrations under 400 ppmv, the least activated material is the most adsorbent.

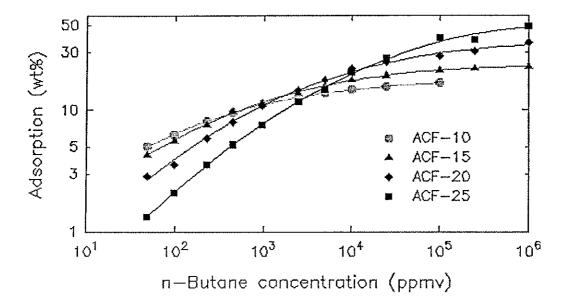


Figure 19: Adsorption isotherms for n-butane in nitrogen on ACF of different degrees of activation. (Data courtesy of J. Economy and K. L. Foster, University of Illinois.)

Although this result may seem counterintuitive initially, it is easily understood when pore configuration and size are considered. Physical adsorption is an equilibrium surface phenomenon involving attraction between adsorbate molecule and pore surface. A molecule can only enter a pore wide enough to admit it; but if the fit is a close one, it will be attracted to both sides of the pore, and thus held more tightly than in a larger pore where the fit is looser. Therefore, narrower pores are filled preferentially; wider pores, despite their larger potential capacity, fill only as increasing adsorbate concentration pushes the equilibrium toward greater adsorption. (6)

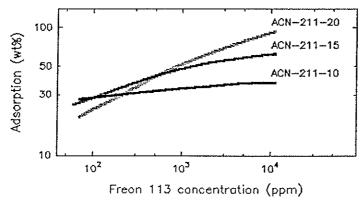


Figure 20: Adsorption isotherms for Freon 113 on activated carbon needled felts.

The same tendency is illustrated in Figure 20 for Freon 113. In this case an activated carbon nonwoven with a specific surface area of 2000  $\rm m^2/g$  (indicated by the "-20" of the article number) adsorbs almost its own weight of Freon at 1% concentration, but well under 20 wt% at 100 ppm. The 1000  $\rm m^2/g$  material, on the other hand, adsorbs little more than 30% at 1% concentration, but still captures almost 30 wt% of the target CFC at 100 ppm.

For a more theoretical description of adsorption, ongoing  $work^{(6-8)}$  continues to confirm that the adsorptive behavior of these materials is well characterized by the Dubinin-Radushkevich equation,

$$W = W_0 \exp\left[-\left(\frac{P_0}{P}\right)^2\right]$$

$$\beta \frac{k}{x_0}$$
(1)

in which W is the volume adsorbed per gram of carbon at partial pressure P,  $W_0$  is the total micropore volume, R is the universal gas constant and T the absolute temperature,  $P_0$  is the saturated vapor pressure of the adsorbate, B is a similarity coefficient relating the free energy of adsorption of the adsorbate with that of a reference vapor, k is a structural factor for the adsorbent, and  $x_0$  is the mean pore half-width.

## SURFACE MODIFICATIONS

Novoloid fibers contain only carbon, hydrogen, and oxygen; and the activated carbon fibers produced from novoloids are about 95% carbon (Table II). Most of the balance is oxygen, present (with small amounts of hydrogen) in carbonyl (quinone), hydroxyl (phenol), and carboxylic groups attached to the carbon and providing a somewhat acidic surface. This surface may be further modified by any of a number of chemical treatments, including ammoniation to yield a basic surface for enhanced adsorption of acids; further oxidation with strong oxidizing acids to increase adsorption of bases; chlorination to maximize surface polarity; and hydrogenation to remove oxygen and produce a non-polar surface with better affinity for normal hydrocarbons. (8)

These reactions involve addition or removal of matter (or both), and thus also affect specific surface area and specific volume (through both weight and pore size) in addition to surface chemistry. The work completed to date is preliminary; further investigation is required to clarify the complex relationships involved. Nonetheless this approach promises clearly to provide yet another set of tools, in addition to control of pore size and physical configuration, for the tailoring of activated carbon fibers and textiles for specific tasks.

#### TEXTILE CONFIGURATIONS

The textile properties of novoloid precursor fibers, carbon fibers produced by pyrolysis in  $N_2$ , and activated carbon fibers are summarized in Table II.

Table II. Typical properties of novoloid and related fibers

Table II. Typical p.	COPCLUACE OF		3 a4 i 4 a a	anwhan
	Cured	Carbon, HTT	Activated	
	<u>novoloid</u>	800°C	ACF-15	ACF-20
Diameter, μm	15	12	10	10
Specific gravity	1.27	1.55	<b> 1.4-1.6 </b>	
Tenacity, g/d	1.3-1.8	<del></del>		
Tens. str., MPa	160-200	500-700	400	350
Elongation, %	30-50	2-3	2.8	2.7
Modulus, GPa	3.5-4.5	20-30	14	12
Carbon cont., wt%	76	95	95	95
Resistivity, $\Omega \cdot cm$	$10^{15} - 10^{16}$	$1 - 3 \cdot 10^{-4}$	$1-2 \cdot 10^{-2}$	$2-4 \cdot 10^{-3}$
Sp. sfc. area, $m^2/g$	<1	<1	1500	2000
TGA stability, °C(*)	305	430	<del></del>	00 —
Moisture regain <sup>(†)</sup>	6	10	37	20

<sup>\*</sup> TGA stability: temperature of onset of heat loss, TGA in air.

As is evident from Table II, the novoloid precursor fibers are suitable for handling by conventional textile processes to make yarns, nonwovens, and woven and knitted fabrics. Activated carbon fibers, on the other hand, are easily converted to wetlaid nonwovens, but their comparative fragility (low toughness) and electrical conductivity present potential problems for spinning, weaving, or needling. Thus an important feature of novoloid fibers as precursors for activated carbon textiles is that the simplicity of activation makes it both practical and convenient to produce activated carbon materials from textile structures which have already been fully formed in the precursor stage.

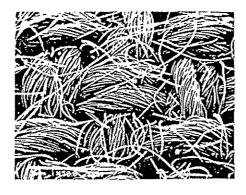


Figure 21: Electron micrograph, activated carbon fabric ACC-507-15. (Courtesy of Center for Ceramic Research, Rutgers University)

<sup>†</sup> Moisture regain: equilibrium moisture content at 25°C, 65% RH.

Figure 21, for example, is an electron micrograph of an activated carbon fabric (ACC-507-15) made by activating a woven novoloid fabric (#507). It is to be emphasized that this figure shows a fabric consisting entirely of activated carbon, and not merely coated or impregnated. Each of the fibers is an activated carbon fiber; and as is quite clear from the figure, the structure of fibers, yarns, and woven fabric has come through the activation process completely intact and functional.

The following list illustrates the great variety of textile structures which have been made hitherto using novoloid fibers, novoloid-based ACF, and the techniques indicated:

# Activated Carbon Fibers and Textile Structures

# Fibers:

Milled fibers, average length 100 μm or less (for molded products, pressed battery electrodes)
Cut fibers (precision cut, for flocking)
Chopped fibers (for molded products, wet-laid nonwovens)
Continuous tow (for precision cutting, break-spinning, etc.)

# Yarns:

Spun yarns, from spun novoloid yarns
Filament yarns, from novoloid filament yarns
Blended yarns, by break-spinning of combined activated
carbon and acrylic or other tows

# Woven fabrics:

Fabric weights from 85 to 450 g/m<sup>2</sup>, in various weaves, from novoloid woven fabrics (see Table III)

## Knits:

Fabrics in numerous weights and constructions, from novoloid circular and warp knits

#### Nonwovens:

Needled felts in weights from 80 to 170 g/m<sup>2</sup>, from novoloid needled felts (see Table III)

Air-laid nonwovens from ACF, cardable glass, and PVC fibers, thermally bonded

Wet-laid nonwovens from chopped ACF and binder fibers (see Table II)

HEPA-like filter media from ACF, submicron glass fibers, and fibrillated binder fibers (9)

# Flocked fabrics:

Prepared by electrostatic flocking of cut fiber onto both permeable and impermeable substrates

## Molded articles:

Molded filter media from ACF and fibrillated binder fibers

Finally, Table III lists properties of representative woven and nonwoven activated carbon fabrics in order to give some sense of what sorts of materials can be made and of how weight, thickness, and strength vary both with one another and with changes in the level of activation. The table thus includes both materials made from the same precursors (fabric 5092 and felt 210) but activated to different levels, and materials made from different precursors but at the same 1500  $g/m^2$  level of activation.

Table III. Activated carbon textiles -- typical properties (\*)

Article number	ACF content wt%	weight g/m²	thickness mm	I <sub>2</sub> adsörp. mg/g	tensile warp kg/5	fill
Woven fabrics (†)						•
5092 (precursor	r)	300	0.75		60	50
ACC-5092-10	100	205	0.66	1300	30	20
ACC-5092-15	100	165	0.60	1500	20	10
ACC-5092-20	100	150	0.55	1700	12	8
ACC-5092-25	100	125	0.54	1900	8	5
ACC-507-15	100	115	0.47	1500	12	10
ACC-519-15	100	300	0.88	1500	30	12
ACC-523-15	100	350	0.95	1500	43	28
Needled felts (\$)						
210 (precursor)		200	2.00		5.0	10.0
ACN-210-10	100	150	1.50	1300		
ACN-210-15	100	120	1.20	1500	0.5	1.0
ACN-210-20	100	100	0.80	2000	0.3	0.5
ACN-157-15	100	90	1.00	1500	0.3	0.5
ACN-211-15	100	155	1.55	1600	1.0	2.0
ACN-305-15	100	170	1.80	1500		
Wet-laid nonwove	<u>ns</u> (**)					
ACP-304	50	50	0.20	630	2	1
STV-505	50	50	0.20	700	5	3
ACP-401	78	22		700		

<sup>\*</sup> The final digits of the article numbers show level of activation.

## APPLICATIONS

In this final section we touch briefly on some of the many applications which have been found for novoloid-based activated carbon fibers and textiles.

<sup>†</sup> Activated carbon fabrics made from woven novoloid precursors.

<sup>§</sup> Activated carbon nonwovens made from novoloid needled felts.

<sup>\*\*</sup> Wet-laid nonwovens made from chopped ACF-15 plus fibrous binders; binders are wood pulp, PVA fiber, and polyethylene fiber, respectively.

Filtration: The adsorbent qualities of activated carbon have long been utilized in a broad variety of filtration applications to remove noxious and/or toxic materials from gases and liquids. Activated carbon fibers and textiles have a number of important technical advantages over conventional granular and powdered activated carbons for filtration applications:

- $\bullet$  High fiber surface-to-volume ratio and direct connection of micropores to the fiber surface significantly shorten diffusion distance and increase speed of adsorption and desorption.
- Pore dimensions and surface characteristics can be tailored to the application.
- Depending on the target material, excellent rates of removal may be obtained even at ppb or ppt concentration levels.
- Fibers can be locked into textile structures, preventing "channeling" and minimizing loss and contamination due to interparticle abrasion.
- Textile structures are often convenient for filter design and assembly; compared to textiles impregnated with powdered carbon, there is less shedding of particulates and no pore blockage by binders.
- Shed particles tend to be fiber fragments with minimum 10  $\mu m$  dimensions, easily trapped in particulate filter media.
- Regeneration by electrical resistance heating may be possible.

Such technical considerations make activated carbon fibers highly useful in specialized filtration applications such as the following, despite their higher cost as compared to granular and powdered activated carbons.

<u>Air filtration</u>: Activated carbon fabrics, laminated to additional filter media for physical support and more efficient particulate filtration, are used in breather filters for computer disk drives to remove such potential contaminants as lubricants and plasticizers which may pose physical or chemical threats to mechanism or media. The activated carbon fiber may be further treated with carbonates to neutralize acid gases, or with polymers such as polyvinyl alcohol to reduce shedding.

Other air filtration applications include simple face masks for suppression of unpleasant odors, and filters to remove tobacco and other smells in autos and homes. Capacity considerations may limit usage in high-volume car cabin filters, but the very fast dynamics of adsorption provide the potential for use in leveling of peak contaminant loads.

Tightening regulations on effluent emissions and workplace contaminants, as well as increased interest in indoor air quality

and "sick building syndrome," will continue to expand the market for materials capable of cleansing air of chemical pollutants.

Solvent recovery: Where airborne concentrations of solvents or other volatile organic compounds (VOC's) are particularly high, recovery of such materials for reuse or efficient disposal may be an attractive and economical alternative to incineration or dilution; recovery may even be required by regulation. The excellent adsorption and desorption dynamics, (10) lack of channeling, and long lifetimes of activated carbon fiber materials make them an attractive choice for systems combining adsorption/desorption cycles and thermal condensation. This is particularly the case when physical space for the installation is at a premium.

Radioactive iodine filtration: Activated carbon fiber filter media have demonstrated high efficiency in removing radioactive isotopes of iodine from the air in nuclear generating installations.

Ozone elimination: Ozone elimination by activated carbon is not, strictly speaking, a filtration application; rather, the carbon surface acts as a site for conversion of adsorbed ozone back to oxygen, through the simple reaction

$$2 \cdot 0_3 \longrightarrow 3 \cdot 0_2$$

Activated carbon textiles show excellent efficiency in ozone removal; the gradual decline in effectiveness over time appears to be the result of slow loss of surface area due to oxidation of carbon by ozone.

<u>Medical applications</u>: Activated carbon fiber nonwovens have been incorporated into bandages and similar wrapping materials for use with malodorous wounds and colostomy bags. Their use has been shown to be particularly beneficial with cancer patients, where odor may lead to increased physical and psychological isolation.

Military applications: Unfortunately the end of the cold war has not reduced, and may in fact have increased, the need for preparedness against chemical warfare. Activated carbon fibers and textiles have been incorporated into a variety of chemical defense garment designs, and have shown good effectiveness when tested against both simulants and live agents. For agents delivered as liquid aerosols, the usual approach is first to present a barrier to the liquid droplets and then to adsorb whatever vapors may penetrate that barrier. Designs have included:

- composite laminates of woven and knitted activated carbon fabrics with PTFE membranes and/or other support layers;
- fabrics woven from blended yarns made by break-spinning of combined tows of activated carbon and acrylic or other fibers;

- air-laid nonwovens made from activated carbon fibers and low-melting binder fibers; and
- flocked fabrics produced by electrostatic flocking of ACF on knitted, nonwoven, or woven substrates.

The use of light-weight knits of activated carbon in suitable composite structures may provide the best combination of flexibility, durability, and heat permeability for this type of application.

Such an approach is not effective against breathable "blood agents" delivered as gases, including hydrogen cyanide and cyanogen chloride; here protection requires a face mask in which the agent is detoxified by catalysis on such media as "whetlerized" activated carbon treated with metals including copper and silver. Activated carbon fibers are easily "whetlerized," and their advantages as filter media (no channeling, ease of assembly, etc.) brought into play.

Industrial safety: A similar application is found in filter cartridges for protection against industrial contaminants and gases. For instance, it has been shown that activated carbon fiber media impregnated with palladium and/or platinum catalyze the oxidation of carbon monoxide (CO) to carbon dioxide (CO<sub>2</sub>); palladium was found to be somewhat more effective than platinum, particularly in conditions of high humidity.

Water treatment: It is unlikely that activated carbon fibers will ever compete economically with granular activated carbon for routine treatment of municipal water supplies or effluents, where cheap total adsorptive capacity is a key factor. For specialized applications, however, such as those involving very low concentrations or particularly dangerous contaminants, the excellent dynamics of adsorption and efficacy at low concentrations and the possibility of tailoring pore size and surface chemistry provide opportunities. Examples include atrazine at ppb levels.

Trihalomethanes (THM, including chloroform) are formed when water contaminated with organic matter is treated with chlorine, and are probable carcinogens. In the United States the Safe Drinking Water Act limits total THM to 100 ppb in public water systems. However drinking water delivered to the household may still contain chlorine, hypochlorite ions, and similar treatment chemicals; these may become the source of new THM's by reacting with organic compounds during cooking or brewing tea or coffee.

A faucet-mounted filter containing activated carbon fiber not only adsorbs THM's, but also eliminates free chlorine and other chlorine-containing compounds by such reactions as:

$$2 \cdot \text{Cl}_2 + 2 \cdot \text{H}_2\text{O} + \text{C} \longrightarrow 4 \cdot \text{HCl} + \text{CO}_2$$
  
 $2 \cdot \text{NaClO} + \text{C} \longrightarrow 2 \cdot \text{NaCl} + \text{CO}_2$ 

A properly designed filter of ACF-20 will remove virtually all the free chlorine (inlet concentration 2ppm) from several hundred liters of water per gram of ACF-20. As with ozone elimination, the process here is one of reaction rather than adsorption and the gradual loss of effectiveness is directly related to reactive removal of carbon (and perhaps also to chemisorption of chlorine on the remaining carbon surface).

Electrical and electronic applications: The electrical conductivity and high specific surface areas of activated carbon textiles lead directly to important applications in electronics and electricity. For instance, the capacitance of a simple two-layer capacitor is linearly related to the surface area of its two electrodes. Activated carbon fabrics with specific surface areas of 2500 g/m², plasma-coated on one side with aluminum for increased conductivity, are used with an organic electrolyte to produce just such capacitors; (11-14) and since very small quantities of such fabrics have very large surface areas, a capacitor 2 cm in diameter and 1 mm thick can have a capacitance of 2/3 farad. Figure 22 is a sketch of such a capacitor. These devices are now in wide use as backup batteries in computers and VCR's, and even for energy storage in solar-powered wrist watches (which must run during the night as well).

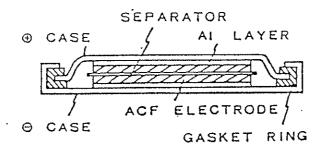
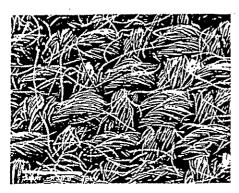


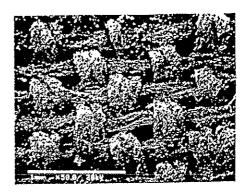
Figure 22: Capacitor with activated carbon fabric electrodes.

Potential related applications now under study include electrodes for lithium and other cells, as well as for large-capacity storage batteries based on new electrochemical technologies and intended for load-leveling, to balance day- and night-time demand on utilities.

Ceramics: The final application to be considered is an unusual one, involving ceramics. Because of their high porosity activated carbon textiles are readily impregnated with metal-containing solutions such as silicon tetrachloride, silicon ethoxide, titanium tetrachloride, or solutions of lead zirconium titanate. Impregnation may be repeated to increase pickup. After drying, the impregnated fabric is next heated at 500 to 550°C in air to burn off the carbon. Calcining at 700 to 800°C, followed by sintering at 1000°C or more, leaves a ceramic replica of the original activated carbon fabric.

This technique has been used to produce silica, titania, and niobium-doped lead zirconium titanate (PZT) replicas of activated carbon textile templates. (15,16) PZT is well-known as a piezoelectric ceramic; such replicas have potential applications in piezoelectric composites for use in hydrophones and other imaging devices. Figure 23 is an electron micrograph of an activated carbon fabric (ACC-507-15); Figure 24 shows the corresponding PZT replica or relic.





Figures 23, 24: Electron micrographs of ACC-507-15 and its PZT ceramic replica. (Courtesy of Center for Ceramics Research, Rutgers University)

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