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ACTIVATABLE COKE FROM CARBONACEOUS RESIDUES

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This application is a continuation-in-part of my previous application, Serial No. 736,972, filed May 22, 1958, now abandoned.

This invention relates to a process for preparing activatable coke from carbonaceous residues such as those obtained from wood, coal, and petroleum.

The use of tar or pitch as a binder is well known in the carbon industry. Tarry and pitch-like materials, however, have hitherto not been seriously considered as a source of base carbon since the material produced therefrom is too dense and lacks the requisite pore structure. Previous attempts to impart a cellular structure to coke made from tars or pitches by adding thereto carbonizing or dispersing agents have not been commercially practical, in general, because of the low yield of activated product obtainable therefrom and because of the processing difficulties normally encountered during activation in such instances.

The recent development of new unit processes in the chemical industry such as the hydrogenation of coal, for example, has increased the availability of tarry and pitch-like by-product materials. In many of these processes the by-product materials are of such uncertain composition and have such unpredictable properties as to render these materials unsuitable as binders for formed carbon products.

It is an object of the present invention to provide a method for producing activatable coke from liquid and solid carbonaceous residues yielding activated carbon having properties comparable to those of activated carbon obtained from coconut charcoal and petroleum acid sludge coke.

It is another object to provide methods for producing activatable coke from liquid and solid carbonaceous residues employing carbonizing agents.

Still other objects will readily present themselves to the skilled artisan upon reference to the ensuing specification and the claims.

The foregoing objects are achieved by providing a carbonaceous material, adding thereto sulfur-containing carbonizing agents, and slowly heating the resulting mixture to a temperature in the range from about 450° C. to about 500° C. so as to expel the volatiles and carbonize the residue.

Carbonizing agents suitable in the practice of this invention include sulfur, sulfuric acid, potassium sulfide, potassium thiocyanate, and the like.

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Neither the kind of carbonaceous residue nor its origin is critical in the instant process. The process as taught herein can be applied to any liquid or solid tarry or pitch-like material. The applicability of this process extends even to pitch having too high an iron or ash content to find utilization in the carbon industry, for example, hardwood pitch.

When the carbonaceous material is in the liquid state it can be mixed directly with the carbonizing agent and heated slowly up to the requisite temperature or the heating can be temporarily interrupted as soon as the material becomes solid, the solid material then subjected to a size reduction operation, and the heating then continued. Both procedures have been followed with substantially the same result.

On the other hand, when carbonaceous material is a solid at room temperature, the material should be comminuted or crushed prior to admixing with the carbonizing agent. Preferably the solid material should be milled to a flour passing through a 100 mesh screen.

In either event, the resulting admixture is slowly heated, usually in the absence of air, to a temperature in the range from about 450° C. to about 500° C. so as to expel the volatile constituents and carbonize the residue.

The thus produced activatable coke can then be crushed to the desired particle size and activated, or it can be pulverized, formed into pellets using a suitable binder, and then conventionally activated with limestone or an oxidizing gas such as steam or flue gas.

The following examples illustrate the present invention.

Example 1

Two 100 gram portions of powdered coal depolymerization pitch were admixed separately with 30 and 90 gram portions of concentrated sulfuric acid diluted with 70 and 56 grams water. The two mixtures were then carbonized by heating slowly (5 to 6 hours) in covered crucibles to 450° C. At this point, the coke yields amounted to 94.4 and 97.6 grams and contained 87.6 and 86.0 percent fixed carbon at 950° C. Both cokes were then crushed through 100 mesh and 20 gram portions of each were mixed with 175 and 172 grams of 20 to 65 mesh limestone (an amount of limestone equivalent to ten times the fixed carbon content of the cokes), placed in crucibles packed in coke and heated to 950° C. to decompose the limestone and activate the carbon with the evolved carbon dioxide. The resulting carbons were then separated from the lime with a 100 mesh screen and tested. The adsorptive capacity of the carbon was determined by exposing weighed samples in a desiccator to carbon tetrachloride vapor. The values reported in Table I show the weight percentage adsorbed at saturation or constant weight, based on the true carbon content.

TABLE I

	450° Coke			Activation Data				
	Yield, Percent	AD ¹	FC, ² Percent	L/FC ³	Activation Yield, Percent	Overall Yield, Percent	CCl Sat., Percent	AD ¹
Pitch Carbonized With—								
No added chemical	59.5	.690	88.0	10	37.7	22.4	10.9	1.28
30% H ₂ SO ₄	94.4	.826	87.6	10	38.4	36.2	68.1	.675
90% H ₂ SO ₄	97.6	.793	86.0	10	28.1	27.4	84.1	.576

¹ Apparent Density.
² Fixed Carbon at 950° C.
³ Limestone to fixed carbon ratio.

It should be noted in Table I that when the pitch is carbonized with sulfuric acid, its coke is readily activated and the resulting carbon adsorbs from 68 to 84 percent of its weight of carbon tetrachloride. In this connection, it is well to note that the activatability of the coke and the coke yield both increase with the concentration of the acid used. This is shown in Table I in the case of coke made with 30 and 90 percent sulfuric acid. On the other hand, when the sulfuric acid is eliminated from the procedure, the resulting carbon only adsorbs 11 percent carbon tetrachloride, its density is much higher and the yield is lower.

Example 2

The same general procedure as in Example 1 was followed, except that 20, 30, 40 or 60 grams of powdered sulfur was mixed with 100 grams of powdered pitch in place of the sulfuric acid. These admixtures were slowly heated, as before, to 450° C. to expel the volatile and carbonize the residue, then crushed through 100 mesh and activated with a 10/1 limestone-fixed carbon ratio. The experimental results are compiled in Table II below.

TABLE II

	450° Coke			Activation Data				
	Yield, Percent	AD ¹	FC, ² Percent	L/FC ³	Activation Yield, Percent	Overall Yield, Percent	CCl ₄ Sat., Percent	AD ¹
Pitch Carbonized With—								
20% S.....	93.4	.893	86.2	10	31.3	29.2	42.5	.881
30% S.....	100.0	.735	81.8	10	34.9	34.9	54.2	.642
40% S.....	101.2	.938	87.2	10	32.4	32.8	70.7	.666
60% S.....	112.3	1.000	81.2	10	27.5	31.0	83.5	.656

¹ Apparent Density.

² Fixed Carbon at 950° C.

³ Limestone to fixed carbon ratio.

These results readily show the advantage of the added sulfur. For nearly the same product yield, the activity of the carbon was increased from 42.5 to 83.5 percent by the simple expedient of raising the sulfur from 20 to 60 parts per 100 parts of pitch.

Example 3

In this case, the powdered pitch was mixed with 5, 10, 20 and 40 parts of pulverized potassium sulfide per 100 parts of pitch, carbonized and crushed as before, but then divided into two portions. One portion was activated directly with an 8/1 limestone-fixed carbon ratio and acid-washed after activation, while the other portion was acid washed before activating with an 8/1 limestone-fixed carbon ratio. The results in Table III show that it is beneficial to remove the salt before activation, but that improved results are possible in either case, especially when compared with pitch carbonized without an added chemical.

TABLE III

	450° Coke			Activation Data				
	Yield, Percent	AD ¹	FC, ² Percent	L/FC ³	Activation Yield, Percent	Overall Yield, Percent	CCl ₄ Sat., Percent	AD ¹
Pitch Carbonized With—								
5% K ₂ S.....	76.6	.990	83.2	8	26.4	21.7	36.2	.825
				W-8	25.5	20.3	55.6	1.070
10% K ₂ S.....	84.4	.812	75.0	8	20.4	18.1	45.9	.720
				W-8	25.0	21.6	69.1	.785
20% K ₂ S.....	96.8	.709	84.7	8	16.0	16.9	69.3	.495
				W-8	27.0	26.1	99.4	.485
40% K ₂ S.....	98.9	.553	77.7	8	9.2	11.2	92.9	.386
				W-8	31.3	31.0	87.8	.501

¹ Apparent Density.

² Fixed Carbon at 950° C.

³ Limestone to fixed carbon ratio.

W=Coke acid washed before activation.

Example 4

The procedure of Example 1 was repeated with hardwood pitch, except the 450° C. coke was crushed through 200 mesh, formed into pellets with more pitch as binder, and then activated with limestone at an 8/1 fixed carbon ratio as indicated in Table IV, below.

TABLE IV

Pitch mix:	Hardwood pitch
Pitch, parts	100
H ₂ SO ₄ , parts	100
Water, parts	23
Coked at 450° C.:	
Yield, percent	74.5
Apparent density (10-14 mesh)	.458
Coke mixed with wood pitch and pelleted:	
Coke, parts	100
Pitch, parts	40
Oil, parts	10
Mixer yield (pitch basis), percent	107.3
Apparent density (green pellets)	.649
Apparent density (calcined pellets)	Fused
Fixed carbon, percent	68.0

Activation of pellets:

40	Lime/fixed carbon	8/1
	Yield, percent	27.0
	Overall yield, percent	29.0
	Activity, percent	97.1
	Retentivity, percent	52.1
45	Apparent density	0.322

In Table IV, and in Table V below the term "Activity" denotes the percent CCl₄ adsorbed by a 10 cm. layer of dry carbon at saturation and 25° C. from pure dry air saturated with CCl₄ vapor at 0° C. and the term "Retentivity" denotes the percent CCl₄ retained by the same sample after pure dry air is passed through the saturated sample for exactly six hours at a linear velocity of 500 cm./min.

The best pelleted carbon made from pitch has characteristics which compare favorably with carbon made from petroleum acid sludge and cocoanut material. This comparison is presented in Table V below.

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TABLE V

	Pitch and 100% H ₂ SO ₄	Sludge	Cocoonut
Activity, percent.....	75.0	75.0	75.0
Retentivity, percent.....	41.5	41.5	45.0
Apparent Density.....	.422	.417	.455
Hardness, max. kg.....	12.0	-----	13.5
Hardness, min. kg.....	4.8	-----	3.0
Hardness, avg. kg.....	8.5	-----	7.4
Lime/Fixed Carbon.....	8.6/1	8.3/1	8.1/1
Yield, percent.....	a 47.5	b 37.5	c 46.5

- a Yield from original pitch.
b Yield from coke.
c Yield from charcoal.

In additional examples of the practice of the invention, coke samples made in accordance with Example 1, 2 and 4 were activated with steam to give activated carbon having substantially the same properties as indicated in the tables. Thus it can be said that the precise method of activation is not critical to the present process.

Example 5

Portions of refined coal tar (1500 grams) and settled wood tar (2100 grams) were placed in glass beakers and mixed with equal amounts by weight of concentrated sulfuric acid. The resulting mixtures were heated to and held at about 150° C. in a ventilated electric oven overnight (approximately 16 hours). This procedure yielded hard, porous, solid residues of black color in both instances.

The solid residues were then rough crushed and packed individually in covered carbon crucibles. The crucibles, in turn, were packed in coke in an alloy box and heated to about 500° C. in an electric muffle furnace.

The resulting activatable residues were then crushed and sized to 6-14 mesh. Portions of the sized activatable residues (about 50 to 60 grams each) were then activated in an atmosphere of steam and nitrogen for about 1 to 2.5 hours at about 950° C. The activator was a cylindrical alloy vessel equipped with lifting vanes, and a steam preheater. During activation the activator was rotated at about 10 r.p.m. and was purged with nitrogen during the heat-up and the cooling.

The data from this example are summarized in Table VI below.

TABLE VI

	Refined Coal Tar			Settled Wood Tar		
Liquid tar, parts by weight.....	100			100		
Sulfuric acid, conc., parts by weight.....	100			100		
Heated 16 hrs. at 150° C., parts by weight.....	147.3			100		
Calcined to 500° C., parts by weight.....	92.5			64.8		
Sized 6-14 mesh, percent yield.....	62.6			71.5		
Sized 6-14 mesh, parts by weight.....	57.8			46.3		
Properties of Activatable Coke:						
Apparent density (6-14 mesh).....	.552			.621		
Fixed carbon (950° C.), percent.....	91.4			85.5		
Fixed carbon (950° C.), parts by weight.....	84.5			55.4		
Activated in steam at 950° C.:						
Time, hours.....	1	1½	2	1	2	2½
Activation yield, percent of 500° coke.....	67.1	51.6	33.9	67.5	40.0	32.4
Overall yield based on tar, parts by weight.....	38.8	29.8	19.6	31.2	18.5	15.0
Overall yield based on tar, but excluding fines loss, parts by weight.....	62.0	47.7	31.4	43.7	25.9	21.0
Properties of activated carbon:						
Activity, percent CCl ₄ adsorbed ¹	34.4	60.8	90.8	24.8	64.5	75.7
Retentivity, percent CCl ₄ retained ²	19.1	29.4	31.9	11.3	28.5	25.6
Apparent density, g./ml.....	.524	.406	.327	.584	.389	.350

¹ The percent CCl₄ adsorbed by a 10 cm. layer of dry carbon at saturation and 25° C. from pure, dry air saturated with CCl₄ at 0° C.

² The percent CCl₄ retained by the saturated sample (1) after pure, dry air is passed through the sample for exactly six hours at a linear velocity of 500 cm./min.

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As is readily apparent from the results reported in Table VI good yields of activatable coke can be obtained in the aforescribed manner.

Example 6

Portions of refined coal tar (213 grams) and settled wood tar (200 grams) were placed in glass beakers and mixed with equal amounts by weight of concentrated sulfuric acid. The beakers containing the admixtures were then covered with sheet asbestos and placed in an electric pot furnace.

The mixtures were then heated to about 450° C. in about 2 hours and were stirred to prevent foaming until solidification. Solidification was observed to take place at about 320° C. with the coal tar and at about 188° C. with the wood tar.

When the foregoing mixtures reached about 450° C., they were removed from the furnace, cooled rapidly and weighed.

A portion (about 50 grams) of each thus obtained activatable coke was then transferred to a carbon crucible which was then packed in coke and heated to about 950° C. in order to determine the fixed carbon content of the activatable coke.

The experimental results, based on 100 parts by weight of original tar are reported in Table VII below.

TABLE VII

	Refined Coal Tar	Settled Wood Tar
Liquid Tar, parts by weight.....	100	100
Sulfuric acid (conc.), parts by weight.....	100	100
After heating to 450° C., parts by weight.....	111	76.8
Fixed carbon, percent.....	78.4	73.0
Fixed carbon at 950° C., parts by weight.....	87.0	56.0

The foregoing results show that at 950° C. the fixed carbon yields for the coal tar and the wood tar were 87 and 56 parts by weight, respectively. These yields compare very well with those reported for coal tar and wood tar in Table VI, i.e., 84.5 and 55.4 parts by weight, respectively, and indicate that in the case of liquid tars it is immaterial whether or not the heating step is interrupted as soon as the tars solidify and whether or not the solidified material is subjected to a size reduction before the

heating is continued to a temperature from about 450° C. to about 500° C.

Example 7

About 100 parts by weight each of 30 medium coal tar pitch, 15 soft coal tar pitch and hardwood pitch were admixed with about 20 parts by weight potassium disulfide. Each resulting admixture was separated into two aliquots. Each aliquot was then contained in a one-liter beaker and placed in an electric pot furnace at room temperature.

One aliquot of each of the above admixtures was then heated to about 400° C. in about 2 hours. Another aliquot of each of the above admixtures was heated to about 450° C. in about 2 hours. During heating the contents of each beaker was stirred continuously so as to prevent frothing. Heating was terminating as soon as the pitch-potassium disulfide mixture reached the desired temperature. The beakers containing the admixture were then removed from the furnace and cooled to room temperature.

The cooled residue in each beaker was crushed to a suitable size and activated by conventional methods utilizing limestone and heating to about 950° C. The fixed carbon content of each aliquot was determined by heating a small portion of the sized material to about 950° C. in a carbon capsule packed in coke. The particle size of the crushed residue and the limestone-to-fixed carbon ratio employed in each instance is indicated in Table VIII below.

Thereafter the resulting carbon product and the limestone were separated by screening and acid washing. The adsorptive capacity of the obtained carbon product was determined by exposing weighed samples of the product to carbon tetrachloride vapors over liquid carbon tetrachloride, at room temperature and in a desiccator. The maximum amount of carbon tetrachloride vapors absorbed by the product was determined by weighing samples of the carbon product before and after the absorption.

TABLE VIII

	30 Medium Coal Tar Pitch		15 Soft Coal Tar Pitch		Hardwood Pitch	
	400° C.	450° C.	400° C.	450° C.	400° C.	450° C.
Pitch, parts by weight.....	100	100	100	100	100	100
K ₂ S, parts by weight.....	20	20	20	20	20	20
Heating Yield, pts./100 pts. pitch.....	101.3	92.9	81.2	77.8	90.5	75.6
Fixed carbon, weight percent.....	77.1	83.3	76.0	83.1	65.2	87.7
Mesh size of product before activation.....	100	100	4-10	4-10	4-10	4-10
Limestone, fixed carbon ratio, by weight.....	8/1	8/1	7/1	7/1	5/1	5/1
Activation yield after screen separation, pts./ 100 pts. pitch.....	24.1	39.1	34.3	3.5	13.2	16.1
Ash, weight percent.....	N.D.	N.D.	95.0	28.1	62.5	42.7
CCl ₄ saturation, percent.....	2.4	6.5	2.2	6.6	2.7	16.6
Activation yield after acid washing, pts./100 pts. pitch.....	10.0	13.1	5.1	1.8	5.6	10.1
CCl ₄ saturation, percent.....	36.8	52.2	10.7	37.8	46.1	49.1

NOTE.—N.D.=not determined.

The data in the foregoing table amply illustrate the necessity of heating the carbonaceous material to a temperature of at least about 450° C. In this manner better activity and a lower ash content in the final product are obtained.

It was also observed that the carbonaceous particles that were heated only to 400° C. in the manufacturing process tended to soften and fuse with the limestone during activation, whereas the carbon particles that were heated to 450° C. under the same conditions did not. This is illustrated by the significant difference in the ash content of the 400° and 450° C. cokes after screening to remove the lime.

The exact mechanism whereby the indicated results are obtained is not known exactly. It is quite evident, however, that the added carbonizing agents increase the porosity and internal surface of the coke.

I claim:

1. A process for making an activatable coke which comprises providing a tarry, pitch-like, carbonaceous residue; mixing therewith a sulfur-containing carbonizing agent selected from the group consisting of sulfur, sulfuric acid, potassium thiocyanate, and potassium sulfide; and slowly heating the thus-formed mixture to a temperature of at least about 450° C. to about 500° C. so as to expel the volatiles contained therein and to carbonize the residue.

2. A process for making an activatable coke which comprises providing a solid, tarry, pitch-like, carbonaceous residue; pulverizing the residue; mixing therewith a sulfur-containing carbonizing agent selected from the group consisting of sulfur, sulfuric acid, potassium thiocyanate and potassium sulfide; and slowly heating the thus-formed mixture to a temperature of at least about 450° C. to about 500° C. so as to expel the volatiles contained therein and to carbonize the residue.

3. The process in accordance with claim 2 wherein the carbonizing agent is sulfuric acid, present in an amount in the range from about 30 to about 100 percent by weight of the residue.

4. The process in accordance with claim 2 wherein the carbonizing agent is sulfur, present in an amount in the range from about 20 to about 60 percent by weight of the residue.

5. The process in accordance with claim 2 wherein the carbonizing agent is potassium sulfide, present in an amount in the range from about 5 to about 40 percent by weight of the residue.

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