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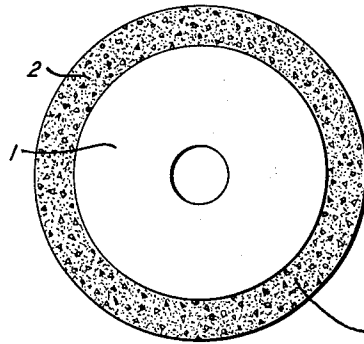
W. O. BAKER ET AL

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ABRASIVE DEVICES

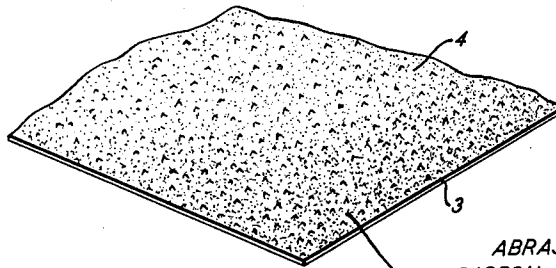
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FIG. 1



ABRASIVE PREDOMINANTLY
CARBON PARTICLES FORMED
BY DEHYDROGENATION IN
SITU OF A SOLID HYDROCARBON
OR MODIFIED HYDROCARBON

FIG. 2



ABRASIVE PREDOMINANTLY
CARBON PARTICLES FORMED
BY DEHYDROGENATION IN
SITU OF A SOLID HYDROCARBON
OR MODIFIED HYDROCARBON

INVENTORS **W.O. BAKER**
R.O. GRISDALE
BY *Edwin B. Cave*
ATTORNEY

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ABRASIVE DEVICES

William O. Baker, Morristown, and Richard O. Grisdale, Short Hills, N. J., assignors to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

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5 Claims. (Cl. 51—295)

This invention relates to abrasive devices.

The abrasive compositions, which constitute the abrasive elements of the devices of the present invention, are formed of sharp-edged particles of a form of carbon, or of carbon containing up to 10 atomic per cent of another normally solid element, which is harder than any form of carbon hitherto reported, other than diamond.

In the accompanying drawing:

Fig. 1 is a plan view of an abrasive cutting wheel formed of the abrasive composition of the present invention; and

Fig. 2 is a perspective view of a flexible abrasive sheet according to the present invention.

The cutting wheel shown in Fig. 1 is formed of a rigid disc 1 formed of a suitable material, such as metal or ceramic, having an annular portion 2 at its circumference over which the disc is tapered to a relatively sharp edge in the manner known in the art. This tapered annular portion, as well as the circumferential edge of the disc is covered with a layer of the abrasive composition bonded to the surface of the disc by means of any of the binders known to the art such as a resinous binder, an inorganic binder or a layer of silicon or germanium in which the abrasive particles are imbedded while the binder is in a fused state.

The flexible sheet shown in Fig. 2 is made up of a flexible backing material 3, such as paper or cloth carrying on its surface a layer 4 of the abrasive composition of the present invention bonded in place with any of the flexible binders known to the art.

The abrasive compositions of the present invention will most commonly be formed substantially entirely of carbon unmodified by the presence of an additional normally solid element and the nature of such carbon and the method of its preparation will first be described.

The abrasive carbon particles of the present invention are produced by the pyrolytic dehydrogenation, in situ, of non-volatile hydrocarbons or hydrocarbon-forming substances.

When branched, high molecular weight hydrocarbons, particularly the cross-linked hydrocarbon polymers, are directly subjected to pyrolysis by heating in a non-oxidizing atmosphere, certain conditions must be observed or else all, or all but a small fraction, of the original material is lost by volatilization of the products of decomposition. The first condition which must be observed is the use of a hydrocarbon possessing an adequate degree of cross-linking in its molecular structure. If this degree of cross-linking is sufficiently high, as in polymerized divinyl benzene, a good yield of carbon, such as 60 per cent, can be obtained directly upon pyrolysis without any other preliminary treatment.

However, in the more usual situation a lower degree of cross-linking is present than the minimum required for a high yield without other treatment. Thus, when polymers of divinyl benzene are subjected to pyrolysis by heating in a non-oxidizing atmosphere, only 6 per cent or 7 per cent by weight of the original material will remain as

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carbon. Polymers which are even less highly cross-linked disappear completely upon heating, leaving no residue.

The yield of carbon upon pyrolysis can be substantially increased by subjecting the hydrocarbon, before pyrolysis, to a treatment which inhibits or retards the loss of carbon by the formation of volatile hydrocarbons during pyrolysis. The formation of volatile hydrocarbons results from the scission of carbon-to-carbon bonds, or depolymerization, in the hydrocarbon as opposed to the scission of carbon-to-hydrogen bonds which is responsible for dehydrogenation. It is therefore the purpose of the treatment before pyrolysis to retard carbon-to-carbon scission while permitting carbon-to-hydrogen scission.

When the hydrocarbon is subjected to pyrolysis after this pretreatment, the predominant reaction is one of dehydrogenation (with carbon rearrangement to take care of the resulting unsaturation) so that ultimately a substantial part of the original carbon skeleton of the hydrocarbon remains, with all but a small amount of the hydrogen removed. By use of such a treatment, yields of carbon up to and in excess of 50 per cent by weight of the original hydrocarbon can be obtained with polymers giving a yield of only 6 per cent or 7 per cent without the treatment. The greatest improvement in yield by the use of this treatment is obtained with those polymers which give the smallest yields without the treatment but some improvement results with all polymers.

A hydrocarbon material which has an intrinsic vapor pressure not greater than 10^{-4} centimeter of mercury at $300^{\circ}\text{C}.$, either initially or after the pretreatment described above, can be subjected to pyrolysis to give a high yield of the essentially carbon bodies of the present invention. As indicated above, hydrocarbons which can be satisfactorily subjected to pyrolysis either with or without pretreatment must initially not only possess a relatively high molecular weight but also have a highly branched or cross-linked carbon skeleton of network structure. The most useful of these substances are the relatively highly cross-linked hydrocarbon polymers.

The effect of extensive cross-linking in retarding loss of hydrocarbon fragments due to carbon-to-carbon bond scission during pyrolysis appears to be twofold in view of what may reasonably be assumed to be the mechanism of pyrolysis. It may be assumed that during pyrolysis carbon-to-carbon bond scission, or depolymerization, occurs simultaneously with carbon-to-hydrogen bond scission, or dehydrogenation. The dehydrogenation creates an unsaturation which tends to lead to further polymerization or cross-linking at the same time that the depolymerization due to carbon-to-carbon scission is occurring. Thus the cross-linked polymer configuration, by merely providing a plurality of bonds linking the various portions of the polymer molecule to the remainder of the molecule, tends to hold these portions in the molecule, even after one or more bonds have been broken, until new bonds are created by dehydrogenation.

The cross-linking appears not only to reduce the splitting off of molecular fragments when carbon-to-carbon bond scission occurs but also to retard the carbon-to-carbon bond scission itself. It is apparent from the bond energies (about 59 kilogram calories per mole for the carbon-to-carbon bond and about 87 kilogram calories per mole for the carbon-to-hydrogen bond) that the breaking of the bonds is not the result of simple thermal dissociation at the temperatures employed for pyrolysis. Therefore the scission appears to be the result of a free radical chain reaction. In a cross-linked polymer network, the network points apparently tend to inhibit propagation of the depolymerizing chain reaction.

However, as indicated above, the mere existence of a highly cross-linked structure in a hydrocarbon polymer is

not necessarily sufficient to prevent an excessive loss of material due to depolymerization during pyrolysis. For a high yield of carbon, it is necessary with most polymers to subject the cross-linked material to a treatment which will result in the further inhibition of the depolymerizing chain reaction, at least during the early stages of the pyrolysis before extensive dehydrogenation has securely bound the bulk of the carbon atoms to the mass being subjected to pyrolysis.

This treatment to inhibit depolymerization involves the introduction of molecular or submolecular atomic groupings which are capable of inhibiting the propagation of free radical chain reactions of the type which appear to be associated with the depolymerization. The introduction of such groupings is most readily and effectively accomplished by baking the cross-linked hydrocarbon body in air or an oxygen-containing atmosphere. The nature of the change which takes place in the hydrocarbon molecules, and which is responsible for inhibiting depolymerization during the subsequent pyrolysis, is not known. This inhibition appears to be the result of the addition of oxygen to the molecules. The evidence indicates that it is oxygen added to side chains or groups, rather than as a linkage in the network structure, which is responsible. The amount of oxygen taken up during the preliminary baking may constitute as much as 15 per cent by weight of the resultant material if the baking is carried on for a prolonged period.

Similar results are obtained by baking the hydrocarbon body in other gases capable of introducing depolymerization inhibiting groups, such as ammonia, nitric oxide, hydrogen sulfide, sulfur dioxide or methyl amine. Instead of forming the inhibiting groups indirectly by baking in a particular atmosphere, the inhibiting groups can be introduced directly by introducing compounds known to be depolymerization inhibitors, such as beta naphthol, the leuco base of 1,4 diamino anthraquinone, t-amyl phenol sulfide, benzaldehyde and other aromatic aldehydes, phenyl beta naphthylamine, hydroquinone, anthraquinone and other aromatic ketones, t-butyl catechol and other substituted phenols, p-phenylene diamine and its derivatives, as well as the mercaptans and the nitro and nitroso compounds. The compounds can be added, in amounts of from about 0.5 per cent to about 5 per cent for instance, by swelling the hydrocarbon bodies in solutions of the compounds in volatile solvents and then allowing the solvents to evaporate.

As indicated above, the presence of inhibiting groups is effective in permitting the production of a coherent, unitary, shaped body containing a relatively high percentage of the carbon originally present, only if the hydrocarbon has an adequately cross-linked molecular structure. The cross-linking of the hydrocarbon is adequate if the hydrocarbon body, prior to the pretreatment referred to above, does not swell to more than five times its original volume in a thermodynamically inert solvent (having no substantial heat of solution), such as benzene or carbon tetrachloride. Preferably the cross-linking is such that the swelling under these conditions is less than 1.25 times the initial volume and the best results are obtained when the swelling is negligible.

In some instances, to be discussed more fully below, a hydrocarbon polymer may be employed which is structurally capable of being polymerized to such a cross-linked state as described above but which, prior to the pretreatment by baking in air or other suitable gas, has not yet achieved this degree of polymerization. During the baking treatment to incorporate depolymerization inhibiting groups, the polymerization may simultaneously be advanced to the point where the cross-linking is sufficient to permit a high yield to be obtained on subsequent pyrolysis. Thus, whether the full requisite cross-linking is achieved before or after pretreatment, the final product in each case possesses the required combination of cross-linking and inhibiting groups to permit dehydrogenation by

pyrolysis to obtain a high carbon yield. In either case, pretreatment by baking renders the product incapable of noticeable swelling in a solvent having no substantial heat of solution.

Hydrocarbon polymers having or capable of achieving the requisite degree of cross-linking may be derived from a variety of sources. The most direct source is from the polymerization of a hydrocarbon monomer or a mixture of hydrocarbon monomers containing olefinic or acetylenic unsaturated bonds and having an average active functionality sufficiently greater than two to permit the required cross-linking. Each olefinic double bond contributes a functionality of two to the monomer and each acetylenic triple bond contributes a functionality of four.

Thus monomers such as divinyl benzene, with a functionality of four, trivinyl benzene, with a functionality of six; divinyl naphthalene, with a functionality of four; vinyl acetylene, with a functionality of six; divinyl acetylene, with a functionality of eight; bis (p-vinyl phenyl) methane, with a functionality of four; or vinyl butadienyl acetylene, with a functionality of ten, may be polymerized to yield hydrocarbon polymers of the required degree of cross-linking for the purposes of the present invention. Similarly, naturally occurring unsaturated short chain hydrocarbon polymers, such as lycopene or beta carotene ($C_{40}H_{56}$), which contain eleven conjugated double bonds in their molecules, may be subjected to further polymerization to produce highly cross-linked materials for use in the production of the abrasive compositions of the present invention.

Mixtures of these polymerizable materials, of functionality greater than two, with one another or with bifunctional hydrocarbon monomers, may be used provided the average available functionality is sufficiently in excess of two to permit the required cross-linking. An average functionality of at least 2.4 is sufficient. The average functionality of a mixture of monomers is computed by multiplying the mol fraction of each monomer in the mixture by the functionality of that monomer and adding together the values obtained for all of the monomers.

The most desirable cross-linked hydrocarbon polymers for the purposes of the present invention are formed from vinyl aromatic hydrocarbons containing at least two vinyl radicals such as any of the isomeric forms of divinyl benzene, trivinyl benzene and divinyl naphthalene or their homologues containing, on the aromatic ring or rings, one or more alkyl substituents, particularly alkyl substituents containing up to six carbon atoms. Of the divinyl aromatic hydrocarbons, divinyl benzene is particularly suitable, particularly when copolymerized with other polymerizable hydrocarbon monomers such as styrene, methyl styrene, ethyl styrene, acetylene, phenyl acetylene, vinyl acetylene, stilbene, indene, vinyl naphthalene or fluorene.

Such copolymers preferably contain at least 20 per cent by weight of the divinyl aromatic hydrocarbon. When the monomer with which it is copolymerized is bifunctional, this minimum of 20 per cent divinyl compound is essential to insure adequate cross-linking. When a divinyl aromatic hydrocarbon is copolymerized with a bifunctional monomer, preferably not more than 50 per cent, and more preferably not more than 40 per cent of the mixture of the two monomers is made up of the bifunctional compound. By maintaining a minimum of 20 per cent of polyfunctional divinyl compound in mixture with a bifunctional monomer, an average functionality, on a weight basis, of at least 2.4 is maintained.

Particularly desirable results are obtained where the polymer is formed entirely of vinyl aromatic hydrocarbon monomers, particularly vinyl benzenes. Such polymers may be formed, for instance, of divinyl benzene alone or in mixture with a monovinyl benzene such as styrene, methyl styrene, ethyl styrene or some other vinyl benzene having, on the benzene ring, one or more alkyl substituents, particularly those containing up to six carbon atoms. A commercially available technical form of

divinyl benzene, containing about 50 per cent divinyl benzene isomers, about 40 per cent vinyl ethyl benzene and the remainder inert diethyl benzene was found well suited for the formation of hydrocarbon polymers to be converted to abrasive carbon.

As indicated above, if the degree of cross-linking is sufficient, high carbon yields can be obtained by the pyrolysis of hydrocarbon polymers which have not been subjected to any depolymerization inhibiting pretreatment. Polymers formed from hydrocarbon monomers having a functionality of at least six, or from a mixture of monomers containing at least 50 per cent by weight of a monomer having a functionality of at least six fall in this class. This is particularly true of such polymers formed from monomers having a molecular structure consisting of vinyl groups attached to a residual hydrocarbon grouping having a hydrogen-to-carbon ratio no greater than one. Aromatic hydrocarbons containing at least three vinyl substituents, particularly trivinyl benzene, are the most effective members of this group.

Copolymers of monomers of this type with hydrocarbon monomers of lower functionality will give decreasing, but high, carbon yields, as the proportion of lower functionality monomer is increased, when subjected to pyrolysis without pretreatment. Pretreatment will, however, increase the yield as indicated above.

Polymerization of the monomers or mixtures of monomers from which the products of the present invention are produced can be accomplished in the conventional manner with either the original monomers or the partially polymerized material, while still plastic, being formed in the desired shape. Thus polymerization is conveniently accomplished by adding 1 per cent by weight of benzoyl peroxide to the material to be polymerized and then heating it to a temperature at which polymerization occurs at a practical rate, as for instance at temperatures between 60° C. and 150° C.

When the hydrocarbon is subjected to pyrolytic dehydrogenation, the carbon which is produced possesses the same shape as the hydrocarbon body from which it is formed. It is therefore desirable that the hydrocarbon be formed in a shape such that the body of carbon which is produced can be conveniently converted to the sharp-edged particles useful for abrasive purposes. This can be done advantageously by forming the hydrocarbon polymer as a film on a smooth surface as of metal or glazed ceramic. After the film has been converted to a continuous film of carbon, it can be stripped from the base in the form of sharp-edged flakes. Polymer films of thicknesses between about .01 millimeter and 2 millimeters can conveniently be used, depending upon the particle size desired in the abrasive. Polymer films of such thicknesses will result in carbon flakes having thicknesses between about .005 millimeter and 1 millimeter.

Sharp-edged particles of smaller size can be produced by the breaking up of these flakes or of carbon bodies of other shape. Abrasive compositions suitable for polishing can be produced by reducing the carbon material to sharp-edged particles capable of passing a screen having 400 mesh per inch or, for finer work, 600 mesh or 900 mesh, corresponding to particle sizes less than about 1.5×10^{-3} inches, 0.75×10^{-3} inches and 0.5×10^{-3} inches.

The hydrocarbon polymers from which the abrasive carbon of the present invention is produced have been described above as derived from hydrocarbon monomers. The hydrocarbon polymers can also be formed from linear or network polymers which contain only carbon atoms in the linear chains or networks but which also contain substituent atoms or radicals containing elements other than carbon and hydrogen, such as oxygen, nitrogen, sulfur or halogens, and which upon heating are converted to cross-linked hydrocarbon polymers. Thus, polyvinyl alcohol, which is an essentially linear polymer, evolves its oxygen in the form of water when heated to

a temperature of 250° C. in a non-oxidizing atmosphere. The unsaturation introduced by the splitting off of the substituents results in extensive cross-linking so that, by the time substantially all of the oxygen has been driven off, as for instance after about fifteen hours at 250° C., a hydrocarbon polymer possessing adequate cross-linking for use in the process of the present invention has been produced.

Similarly, polyvinylidene chloride and polyvinyl chloride, both essentially linear polymers, evolve HCl when heated in inert or non-oxidizing atmospheres or in the presence of dehalogenating agents and yield cross-linked hydrocarbon polymers suitable for the purposes of the present invention.

Examples of other cross-linked polymers which contain elements other than carbon and hydrogen and which are converted to cross-linked hydrocarbon polymers upon heating in a non-oxidizing atmosphere are the polymers of vinyl acrylic acid, chlorovinyl acrylic acid, propenyl ethynyl carbinol, propenyl ethynyl ketone, vinyl ethynyl ketone, hex-3en-5yn-2ol and hex-3en-5yn-2one.

Regardless of the method of preparation, the hydrocarbon polymer may have its carbon yield increased by baking in air prior to pyrolysis. This baking in air, or equivalent gases as set forth above, can be carried out at a temperature between 200° C. and 300° C. and preferably at 250° C. The effectiveness of this baking increases with an increase in the time for which the baking is continued. Although it is possible to obtain a substantial increase in the yield of carbon residue by air baking for as little as two hours, more substantial increases in yield are obtained if the baking is continued for at least four hours. For the greatest increases in yield, the baking is continued for longer periods of, for instance, twenty-four hours or one week or even two weeks.

The pyrolytic dehydrogenation of the hydrocarbon material, with or without pretreatment by baking in air, is carried out in a non-oxidizing atmosphere, at least when the temperature rises above 300° C., in order to prevent loss of carbon by oxidation. The most suitable atmosphere for this purpose is nitrogen at atmospheric pressure, although superatmospheric or subatmospheric pressures may be used if desired. Other atmospheres which are non-oxidizing, such as helium, hydrogen or a sufficiently high vacuum, may be used if desired.

The hydrocarbon bodies are brought gradually to the maximum temperature of pyrolysis so as to allow the gradual release of the gases which are developed and thus prevent destruction of the bodies. It has been found that a temperature rise of about 200° C. per hour between about 300° C. and the maximum temperature yields desirable results. Obviously the bodies may be heated more slowly if desired, as for instance at an average rate of about 5° C. per hour. A more rapid rate of heating, up to about 500° C. per hour, may also be used. It is apparent that, although the temperature increase is preferably made continuous, it can also be brought about by stepwise increases, for instance of the order of 25° C. to 100° C.

The residual amount of hydrogen remaining in the final carbon product is dependent upon the maximum temperature to which the bodies are brought during pyrolysis for a substantial period of time. A product consisting of at least 99 per cent carbon can be produced by carrying the pyrolytic temperature to 850° C. and maintaining the material at this temperature for one-half hour or more.

In a typical product subjected to pyrolysis at a temperature increasing at the rate of 200° C. per hour until a temperature of 900° C. was reached and maintained at that temperature for one-half hour, the hydrogen content was found to be 0.64 per cent by weight. After being maintained at 1000° C. for one hour, the hydrogen content was reduced to 0.36 per cent. The hydrogen content was reduced further to 0.23 per cent

by heating one hour at 1100° C. to 0.12 per cent by heating one hour at 1200° C. and to between 0.02 per cent and 0.01 per cent by heating one to three hours at 1300° C. These values represent a hydrogen content of one hydrogen atom per twenty-three carbon atoms in the product heated to 1000° C. and one hydrogen atom per four hundred to eight hundred carbon atoms in the product heated to 1300° C.

The preparation of carbon by in situ dehydrogenation of cross-linked hydrocarbons is more particularly described and claimed in the copending application of W. O. Baker and R. O. Grisdale, Serial No. 223,633, filed April 28, 1951. This application is now United States Patent 2,697,028, issued December 14, 1954.

The hardness required for purposes of the present invention is obtained when the hydrogen content has been reduced to not more than 1 per cent of the weight of the carbon. Preferably the hydrogen content is reduced to less than 0.5 per cent. The dehydrogenated material which is produced is a lustrous, hard, homogeneous, coherent substance with an extremely smooth surface.

X-ray diffraction patterns and other observations indicate that the carbon is less graphitic and more diamond like in its atomic arrangement than any other form of carbon hitherto reported. This atomic arrangement possesses extraordinary stability in that, unlike other forms of pyrolytic carbon, it is not converted to graphite by heating to 2400° C. for several hours.

The preparation of carbon containing a small amount of residual hydrogen has been described. As indicated above, the abrasive carbon of the present invention may be prepared so that it also contains up to 10 atomic per cent of an additional normally solid element. This additional element has no substantial effect upon the properties of the carbon insofar as its use for the purposes of the present invention is concerned.

As examples of such additional elements may be mentioned silicon, boron, phosphorus, silver, titanium, aluminum, bismuth, germanium, tin and other metals and metalloids. By the formation of the polymer, which is to be dehydrogenated, from monomers which contain the additional element as well as carbon and hydrogen, the pyrolytic product containing both carbon and the additional element can be produced.

For instance, silicon can be introduced into the abrasive carbon particles by forming the carbon from a polymer formed from a monomer or monomer mixture containing silicon. Examples of such silicon-containing monomers are the polyallyl silanes, such as tetraallyl silane, methyl triallyl silane, dimethyl diallyl silane, which may be polymerized alone or in mixture with one another or with a polymerizable hydrocarbon monomer such as divinyl benzene or trivinyl benzene. Other such monomers are the silyl styrenes, such as trimethyl silyl styrene, triethyl silyl styrene or other trialkyl silyl styrenes, which should be copolymerized with another monomer of higher functionality, such as divinyl benzene, trivinyl benzene, tetraallyl silane, methyl triallyl silane or dimethyl diallyl silane. The preparation of carbon products containing silicon by in situ dehydrogenation of cross-linked polymers is more particularly described and claimed in the copending application of W. O. Baker, R. O. Grisdale and F. H. Winslow, Serial No. 223,634, filed April 28, 1951. This application is now United States Patent 2,697,029, issued December 14, 1954.

The dehydrogenation of the polymers containing the additional element is carried out under the same conditions as described above for the hydrocarbon polymers.

The invention has been described in terms of its specific embodiments and, since certain modifications and equivalents may be apparent to those skilled in the art, this description is intended to be illustrative of but not necessarily to constitute a limitation upon the scope of the invention.

What is claimed is:

1. An abrasive device having an abrasive surface formed of a plurality of sharp-edged particles of lustrous, hard, smooth, homogeneous carbon, held in place by a binder, said particles of carbon being fragments of a carbon body produced by baking, in an oxygen-containing atmosphere at between 200° C. and 300° C., a solid body consisting of a cross-linked hydrocarbon polymer incapable of swelling in benzene to more than 1.25 times its original volume, said polymer being selected from the group consisting of polymerized trivinyl benzene, polymerized divinyl benzene, polymerized vinyl acetylene and the copolymer of divinyl benzene with a monovinyl aromatic hydrocarbon, and dehydrogenating said baked polymer body in situ by heating it at a temperature of at least 850° C. in a non-oxidizing atmosphere until its hydrogen content is not more than .5 per cent by weight of the carbon.

2. An abrasive device as defined in claim 1 wherein the polymer is a copolymer of divinyl benzene with ethyl vinyl benzene.

3. An abrasive device as defined in claim 1 wherein the polymer is polymerized divinyl benzene.

4. An abrasive device having an abrasive surface formed of a plurality of sharp-edged fragments of a lustrous, hard, smooth, carbon material held in place by a binder, said carbon material having been formed by thermally dehydrogenating, in situ, a solid body consisting of a cross-linked polymer, at a temperature of at least 850° C. in an inert atmosphere, until its hydrogen content is reduced to not more than 1 per cent by weight of the carbon, said polymer being a polymer of trivinyl benzene, said polymer prior to dehydrogenation having an intrinsic vapor pressure not greater than 10^{-4} centimeter of mercury at 300° C.

5. An abrasive device having an abrasive surface formed of a plurality of sharp-edged fragments of a lustrous, hard, smooth, carbon material held in place by a binder, said carbon material having been formed by thermally dehydrogenating, in situ, a solid body consisting of a cross-linked polymer, at a temperature of at least 850° C. in an inert atmosphere, until its hydrogen content is reduced to not more than 1 per cent by weight of the carbon, said polymer being a polymer of vinyl acetylene, said polymer prior to dehydrogenation having an intrinsic vapor pressure not greater than 10^{-4} centimeter of mercury at 300° C.

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