

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
17 June 2004 (17.06.2004)

PCT

(10) International Publication Number
WO 2004/050554 A1

(51) International Patent Classification⁷: **C01B 31/00**,
C09C 1/44, 1/46, C01B 31/02

(21) International Application Number:
PCT/US2003/040060

(22) International Filing Date:
21 November 2003 (21.11.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/429,422 27 November 2002 (27.11.2002) US

(71) Applicant (for all designated States except US): **THE LUBRIZOL CORPORATION** [US/US]; 29400 Lakeland Blvd., Wickliffe, OH 44092-2298 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BURRINGTON, James, D.** [US/US]; 6858 Bramblewood Lane, Mayfield Village, OH 44143 (US). **JOLLEY, Scott, T.** [US/US]; 7094 Victoria Drive, Mentor, OH 44060 (US).

(74) Agents: **LAFERTY, Samuel, B.** et al.; The Lubrizol Corporation, Patent Dept./Mail Drop 022B, 29400 Lakeland Blvd., Wickliffe, OH 44092-2298 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SUBSTRATES WITH MODIFIED CARBON SURFACES

(57) Abstract: A process for functionalizing a carbon surface and the product thereof is disclosed. The first reactant used contains one or more electron withdrawing groups that thereafter can be reacted with other compounds. The reaction product has enhanced dispersability, interaction with other media, or other utilitarian uses, e.g. a reactive surface. The reaction product is then incorporated into an elastomeric or thermoplastic composition; it can be dispersed in a liquid media such as an ink, coating, or lubricant; or it can be used as a solid in applications such as a filtering media.

WO 2004/050554 A1

TITLE: SUBSTRATES WITH MODIFIED CARBON SURFACES

5

Field of the Invention

Substrates with carbon surfaces such as carbon black, carbon fibers, graphite, and activated carbon are modified by reacting with a reactant having at least one double bond and one or more electron withdrawing groups, e.g. maleic anhydride. This reaction is anticipated to create significantly more reactive groups (relatively)
10 on the carbon surface that can be functionalized (if desired) by having a nucleophilic group in the functionalizing agent. These functionalized materials can be used in composites, filtration media, coatings, inks, etc.

Background of the Invention

Carbon black and related substrates having surfaces rich in carbon, e.g. graphite, and carbon fibers, have been considered as relatively non-reactive with
15 most chemical compounds. Silica surfaces which, are rich in hydroxyl groups (also called silanol groups), have been functionalized with a variety of reactants to enhance the interaction of silica with a variety of continuous media such as elastomers and solvents. Some research has been conducted on oxidizing carbon
20 rich surfaces to create carbonyl and carboxy groups on the surface, which would react with nucleophiles. While this work was successful at oxygenating the surface, the physical properties of the substrates were typically also modified during the reactions at elevated temperatures or using strong oxidants such as peroxide or ozone.

25

Summary of the Invention

Carbon rich surfaces can be reacted with compounds of Formula I:

$X_1X_2C=CX_3X_4$ or Formula II: $X_1C(H)=O$; wherein X_1 , X_2 , X_3 and X_4 are independently selected from H, an alkyl of 1 to 4 carbons, or an electron withdrawing group, wherein at least one of X_1 , X_2 , X_3 and X_4 is a known electron
30 withdrawing group, said electron withdrawing groups being characterized by having a $\sigma_p > 0$. where σ_p is the $\log(K'/K_0')$ where K' is the equilibrium constant for the ionization of a para substituted benzoic acid with the particular group and K_0' is the

equilibrium constant for the ionization of benzoic acid in water at 25°C, under conditions such as elevated temperatures to effectively bond a significant portion of the compounds of Formula I or II to the carbon surface. This effectively places X₁, X₂, X₃ and/or X₄ on the carbon surface where they can serve as a point of chemical bonding with nucleophilic reactants. Preferred reactants are maleic acid or anhydride, methyl acrylate, itaconic acid, acrylic acid, glyoxylic acid, the hemiacetal of the methyl ester of glyoxylic acid, and methyl glyoxylate.

Depending on the particular application (embodiment) desired the first reaction product can be further reacted with nucleophilic compound(s) that carry or contain particular reactive groups for further reaction or utility.

A significant application can be a filler in a elastomeric or thermoplastic composite where the carbon rich surface is part of a carbon based filler for the elastomer or thermoplastic. Other applications include dispersing the substrate with a carbon surface in an ink, coating, or a lubricant; or using the substrate with a carbon surface as a filtering media.

Detailed Description of the Invention

The carbon surface can be any form of condensed carbon. The substrate supporting the carbon surface can also be carbon or carbon based or it can be another support material. In most embodiments the substrate is substantially the same material as the surface, e.g. carbon black, graphite, carbon fibers, activated carbon. Desirably the carbon surface must be at least one molecular layer thick if the entire substrate is not carbon. In most embodiments the carbon on the surface constitutes at least 75 weight percent, more desirably 80 and preferably 85 weight percent of the surface. If the substrate is to be carbon based desirably at least 50 weight percent, more desirably 70, and preferably at least 80 weight percent of the substrate is carbon. In a narrowed embodiment the carbon substrate is not carbon black and is not coal.

A general listing of condensed carbon includes particulate carbon such as carbon black and soot, graphite, diamond, carbon fibers, activated carbon, charcoal, activated charcoal, carbonized surfaces e.g. partially carbonized coconut shells, carbon nanotubes, carbon nanoparticles, graphitic nanoparticles, and carbon-containing fullerenes, such as C₆₀. The carbon can be amorphous, crystalline, or a

mixture of amorphous and crystalline. The crystalline portion can be three-dimensional crystals, such as diamond, or two-dimensional crystals, such as graphite. The carbon if it constitutes a major portion of substrate can be particulate, granules, chunky, fibers, or rods (e.g. anodes) etc.

- 5 The carbon surface is desirably treated with a reactant of Formula I: $X_1X_2C=CX_3X_4$ or Formula II: $X_1C(H)=O$ wherein X_1 , X_2 , X_3 and X_4 are independently selected from H, an alkyl of 1 to 4 carbons, or an electron-withdrawing group, wherein at least one of X_1 , X_2 , X_3 and X_4 is a known electron-withdrawing group, said electron withdrawing groups being characterized by having
- 10 a $\sigma_p > 0$, where σ_p is the $\log(K'/K_0')$ where K' is the equilibrium constant for the ionization of a para substituted benzoic acid with the particular group and K_0' is the equilibrium constant for the ionization of benzoic acid in water at 25°C. Desirably the molecular weight of each of the electron-withdrawing groups X_1 , X_2 , X_3 and X_4 is less than 100 grams/mole and the molecular weight of the entire molecule of
- 15 Formula I or II is less than 400 and more desirably less than 200 grams/mole.

Desirably in one narrowing embodiment the carbon substrate is neither carbon black nor coal when the reactant is Formula I or Formula II (with glyoxylic acid, methyl ester of glyoxylic acid and the hemiacetal of the alkyl glyoxylate being possible exceptions).

- 20 Preferred molecules for Formula I are maleic acid, maleic anhydride, alkyl or alkenyl substituted maleic acid or anhydride, and the diels-alder adduct of dienes or polyenes with maleic anhydride or maleic acid, such as nadic anhydride or nadic methyl anhydride. Alternatively it can be acrylic acid, methacrylic, other C_2 - C_4 alkyl substituted acrylic acid, itaconic acid, or C_1 - C_4 substituted itaconic acid, or C_1 -
- 25 C_6 alkyl esters or partial esters of the specified acids.

Preferred molecules for Formula II are glyoxylic acid or esters thereof, derived from reacting glyoxylic acid and C_1 - C_4 alcohols and the hemiacetals of C_1 - C_4 alkyl esters of glyoxylic acid. These have a carbonyl double bond.

- X_1 , X_2 , X_3 and X_4 are desirably selected from carboxylic acid, C_1 - C_{10} esters and salts of carboxylic acids. When Formula I is an anhydride of dicarboxylic acids, two of X_1 , X_2 , X_3 and X_4 combine to form the anhydride. X_1 , X_2 , X_3 and X_4 can also be or contain ester, amide, nitrile, nitro, keto, and aldehyde groups.
- 30

To make the reaction product one applies the reactant of Formula I or II to the surface of the carbon and applies heat. The reaction can be carried out neat using any gaseous environment such as air or inert gas (e.g. argon or nitrogen), or using a liquid solvent (either polar e.g. water or nonpolar), optionally with catalysts present to promote a faster or more effective chemical reaction between the reactant of Formula I or II with the carbon surface. Typical catalysts are Lewis (e.g., BF_3) or Bronsted (e.g., H_2SO_4) acids.

A preferred method is to apply the compound of Formula I or II rather uniformly to the carbon surface by a spray addition, metering, or bulk addition (optionally mixing to further disperse) and then heat the carbon surface and reactant for a few seconds or minutes to several hours at a temperature from about 60°C to about 500°C and preferably from about 100 to 350°C , and most preferably from about 150 to about 300°C . Desirable reaction times are from a few seconds or minutes to one or more days (24 hours or more), depending on the reaction temperature.

As a more efficient process, the carbon black and Formula I or II are fed into a heated zone of a mixing vessel as an aerosol; Formula I or II vaporizes and reacts with the carbon black at temperatures between 200 and 500°C , more preferably 350 to 450°C for seconds to minutes of residence time in the heated zone. The carbon black could be any commercially produced material, or it could be a stream from the carbon black production process -- while it is still very hot and before being quenched. The heated zone could be in a continuous feed reactor, and the ratio of carbon black to Formula I or II might be similar to those used in the batch process with excess Formula I or II -- so weight ratios of Formula I or II to carbon black of $1:1$ to $1:20$, more preferably between $1:5$ and $1:10$, depending upon the adjustments in residence time and temperature and desired characteristics of the product.

The reaction product of a reactant of Formula I or II with a carbon surface can be characterized with (photoacoustic) infrared analysis (PA-FTIR), solid state proton NMR, X-Ray Photoelectron Spectroscopy (XPS), solvent extraction, and/or thermogravimetric analysis. It is generally observed that new infrared peaks and NMR peaks appear after the reaction, a significant portion (usually not all) of the

reactant of Formula I or II is no longer extractable with appropriate solvent extraction techniques and the reaction product, when tested by thermogravimetric analysis, loses weight at different (higher) temperatures than a simple blend of the reactant of Formula I or II and the same carbon surface. These analyses indicate that
5 some form of chemical reaction or physical interaction has occurred between the carbon surface and the reactant.

The carbon surface treated with a reactant of Formula I or II can be further reacted with a nucleophile of the formula R'-Nu, where R'Nu contains one or more nucleophilic group(s) known to react with the electron withdrawing groups of X₁,
10 X₂, X₃ and/or X₄. Said nucleophilic groups include NH₂, NHR, NR₂, OH, SH, SR, PR₃ (or -PR₂), P(OR)₃ (or -OP(OR)₂), NRNHR, NRNR₂, NROR and OOR or any anionic form thereof where R and R' are independently hydrogen, a hydrocarbyl group (optionally being a polyether or polyamine group), a cation containing group, a di, tri or polysulfidic linkage, or combinations thereof. A preferred R'-Nu is
15 ethylene diamine or a polyamine derived from ethylenediamine such as H-[NH-CH₂-CH₂]_n-NH₂ where n=2-6. A broader group of R'-Nu would be the alkylene polyamines represented by the formula R-N(R)- (Alkylene-N(R))_n-R where n can vary from 1-7 or 1-10, each R is independently a hydrogen atom, a hydrocarbyl group or a hydroxy-substituted hydrocarbyl group having up to 30 or 50 carbon
20 atoms, and "alkylene: refers to 1-6 or 1-18 carbon atoms in a linear or branched form. Commercial products of these formulas include these structures along with variants thereof. For example E-100 from Dow Chemical Company of Freeport, Texas has about 22% tetraethylenepentamine and 77% pentaethylenehexamine. A Union Carbide product known as HPA-X[®] includes cyclic condensation products
25 along with higher analogs of diethylenetriamine and triethylenetetramine. The nucleophile can also be a polyether and potassium hydroxide. This is a preferred nucleophile in some embodiments when Formula I is maleic acid or anhydride. The nucleophile can be a coupling aid or agent between the substrate with a carbon surface and another chemical compound e.g. elastomer, plastic, solvent, carrier etc.
30 A coupling aid or agent is generally defined as a material that has two attractions or can chemically or physically bond to two different materials together. Generally it is anticipated that one nucleophilic portion of the nucleophilic compound will be

attracted or chemically bond to one of X₁, X₂, X₃ and/or X₄ on the carbon surface and another portion of the nucleophilic compound (if it is functioning as a coupling aid) will be attracted to or bond to another chemical material, e.g. an elastomer, plastic, solvent etc.

5 As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

10 (1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical);

15 (2) substituted-hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

 (3) hetero substituents, that is, substituents which, while having a
20 predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the
25 hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

 The substrates with a carbon surface can be used as a media or as a filler (optionally a reinforcing filler) in a variety of applications. The reactant of Formula I or II could be characterized as containing one or more electron-withdrawing
30 groups. The electron withdrawing groups X₁, X₂, X₃ and X₄ create additional reactive sites on the carbon surface without requiring harsh conditions that are typically required to oxidize carbon surfaces in the absence of a reactant. The

relatively mild reaction conditions under which the reactant of Formula I or II is added to the carbon surface allows chemical modification of the carbon surface while minimizing changes in the properties below the carbon surface (i.e. in the substrate). The properties below the carbon surface may include things like morphology, particle size, porosity, density, crystallinity, and the presence or
5 absence of heteroatoms other than carbon and hydrogen. It would be desirable to leave all of these substrate properties unchanged while adding the reactants of Formula I or II to the carbon surface of a substrate.

Of particular interest is an embodiment where the substrate with a carbon
10 surface is used as a filtration media to 1) remove a component, 2) add a component, or 3) exchange a component from a media. In this particular embodiment a liquid media would include a gaseous material or a flowable solid (liquid-measure type). The substrate with a carbon surface could be a particulate carbon such as carbon black or a larger size substrate such as activated carbon or charcoal. The substrate
15 could be suspended in a media or used as a packed bed, column or filter media. The reaction product of the carbon surface and the reactant of Formula I or II could be the chemically active part of the filtration media or the reaction product can be reacted with a nucleophilic compound as described above to add another functional group to the filtration media.

20 A preferred embodiment of the use of the reaction product of a carbon substrate with a reactant of Formula I or II would be as a filtration media for removing trace contaminants and/or metals from and aqueous media, a hydrocarbon fuel, or a hydrocarbon lubricant. Hydrocarbon fuels would include but not be limited to gasoline, natural gas, diesel fuel, and jet engine fuel. Lubricants would
25 include lubricants formulated in part of completely with the various American Petroleum Institute (API) group I-V basestocks. The reaction product could additionally be reacted with the various nucleophiles already described to enhance the ability of the filtration media to remove, contain, complex or exchange for the contaminant or metal to be removed in the filtration step.

30 The filtration media can be used to partially or completely remove various compounds or atoms, not limited to cations, salts, complexes of metals with various hydrocarbyl groups etc. In a preferred embodiment the filtration media is used to

remove transition metals as defined in chemical dictionaries. A preferred group of transition metals are those with atomic numbers from 21 to 29 inclusive. A preferred embodiment is the removal of copper or copper containing species from fuels including but not limited to jet fuels. A particular application is the filtration to
5 remove the amount of copper, optionally as salt, free ions, complexed ions etc, from jet fuel where it can exist as a non-desirable contaminant. In later shown examples a copper compound is removed from Isopar G to simulate how the filtration media would remove various copper compounds to low levels such as below 50, 20, 20 or 5 ppb of copper from jet fuel.

10 Another embodiment is to use the modified carbon surface and its corresponding substrate, either modified only with the reactant of Formula I or II, or further reacted thereafter with a nucleophilic compound to 1) aid in the dispersability of the substrate with a carbon surface in another media or 2) change the interaction of the carbon surface with the media after being dispersed (either
15 physical or chemical interaction with the media, e.g. an elastomer, plastic, solvent etc.). In these applications the carbon surface modification would somehow make the substrate with the carbon surface more dispersable or more effective at interacting with another media such as the continuous media or other dispersed media. Applications include using the substrate with a carbon surface in an ink,
20 coating, fiber-reinforced plastic, compounded elastomer, compounded plastic, etc to make an improved product. Some of these compositions would desirably be water-based for environmental reason, such as inks and coatings, while others might be use solvents other than water. If the substrate with a carbon surface is a fiber, then the reaction product of the substrate with a carbon surface, the reactant of Formula I or
25 II and optionally further reacted with a nucleophilic compound can be one of the fiber component(s) of a fiber-reinforced composite. It is possible for the reactant of Formula I or II and/or its subsequent reaction product with a nucleophilic compound to function both as a dispersing and a coupling aid in some situations.

In elastomer compositions formulated in the rubber industry it is common to
30 specify the ingredients based on parts by weight per 100 parts by weight of rubber (phr). A very common form of rubber is derived from polymerizing conjugated diene monomers having from about 4 to 8 carbon atoms and optionally up to one

heteroatom per monomer, such as isoprene, butadiene, or chloroprene. Sometimes a conjugated diene monomer such as butadiene is copolymerized with at least one other monomer such as styrene to form a copolymer, terpolymer etc. depending on the number of comonomers. Natural rubber is a rubber derived from polymerizing isoprene. Generally to get elastomeric properties from such polymers with significant amounts of repeating units from conjugated dienes, it is desirable to have at least 30 weight percent of the repeating units derived from a conjugated diene., more desirably at least 40 weight percent. Substrates having carbon surfaces, e.g. carbon black, are generally used in elastomers compositions at concentration above 1 phr, and more desirably above 20 phr and preferably above 30 phr. Coupling agents or aids (couplers) that potentially can enhance the interaction between the rubber and the carbon surface are generally used above the 0.5 phr concentration and more desirably above 1 phr. A preferred coupler would desirably have an amine group to react with X₁, X₂, X₃ and/or X₄, and either a thiol or polysulfidic linkage that might couple to unsaturation in a rubber compound. A more preferred coupler would also have a carbonyl group such as an ester or amide linkage. Such a coupling agent could be formed from a first amino compound and a second compound, said second compound having both a group that can couple through a condensation reaction with said first amino compound and another group being a thiol, which can, optionally, be converted to a polysulfidic linkage. Synthesis of such a compound is disclosed in copending World application US 01/09290 filed March 22, 2001, which is hereby incorporated by reference for its teachings on thiol or polysulfidic compound that might be used as coupling aids. A preferred second compound is 3-thiopropionic acid methyl ester, where the resulting coupling agent can possibly be reacted with elemental sulfur to form a second coupling agent with a polysulfidic linkage in place of the thiol group.

A desirable amount of the above described coupling agent(s) is generally from about 0.07 to about 300 parts by weight per 100 parts by weight of carbon, more desirably from about 0.5 to about 10 parts by weight per 100 parts by of weight of carbon. The amount of coupling agent generally will vary with the amount of carbon surface area per gram, which can vary significant, depending on

whether one is describing a high surface area carbon black or a low surface area graphite.

Examples

Examples 1-7: Treated carbon black N234, Carbon black and solid maleic anhydride (or another reactant compound with electron-deficient unsaturation) are reacted, either neat or in a slurry of an appropriate solvent, at a temperature and time such that a substantial amount of free maleic anhydride has become reacted or otherwise strongly bonded to the carbon black. In an embodiment with simple stirred reactors temperatures are generally 100-250°C, more preferably 150-230°C. Preferred times are 1 to 36 hours, more preferably, 12 to 24 hrs. After reaction, the solids are washed with acetone and filtered to remove any free reactant. Thus the amount of reactant left on the solid form of carbon should be based on the % wt. reactant column in TABLE 1 rather than the treat rate. Each of the Examples 1-11 showed 3 thermogravimetric analysis features at about 200°C, 320°C, 550°C, which are not present in the carbon controls or samples which had been impregnated with maleic anhydride in solvent and dried, but not heated. The latter gave a large peak at 66°C, which is not present in any of the samples from Ex 1-6. These products also contained more surface oxygen (based on XPS analysis) than the carbon black starting materials. The solid state proton NMR spectrum of this product has a broad peak between 2-3 ppm, and this is what would be expected for the reaction of maleic anhydride with a double bond on the carbon black -- however there are several possible products for this reaction. The PAS-FTIR spectrum shows a peak at 1805 cm^{-1} , and this is the peak associated with the maleic anhydride carbonyl; hence the product contains this type of functional group.

The specific reactants and conditions are shown in Table 1 below. N234 is available from Engineered Carbons, Inc in Borger, Texas, and has a reported particle diameter of 21 nm, a nitrogen surface area of about 125 m^2/g and is used for high reinforcement in rubber compounds. The graphite used was Graphite 3442, a graphite flake from Asbury Graphite Mills, Inc having 99 wt.% passing through a 325 mesh screen.

TABLE 1.

Reactions of Carbon Black (CB) and Graphite (G) with Maleic Anhydride (MA), Itaconic Anhydride (IA), Succinic Anhydride (SA) or Methacrylic Acid (MAA).

(^a= atomic %, by XPS); ^b calculated from %O; ^c(f)=fluffy CB; otherwise, pelletized CB); ^d % wt by gravimetric analysis.

5

Ex. No.	Carbon	Reactant (wt/wt Carbon)	Temp, C	hr	%O ^a	% wt reactant ^b
Control A	N234 CB	none	(Control for Ex 1-2, 4-7, 9-11)		2.5	0
Control B	G 3442	none	(Control for Ex 3)		4.1	0
Control C	N234 CB	none	(Control for Ex 8)		1.6	0
1	N234 CB(f)	MA(1/10)	200	24	4.2	4.6
2	N234 CB	MA (1/10)	200	24	5.0	6.8
3	G 3442	MA (1/10)	200	24	5.4	3.5
4	N234 CB	MA (1/100)	200	24	-	-
5	N234CB	MA (1/5)	200	24	7.1	12.5
6	N234CB	IA(1/10)	200	24	4.4	5.2
7	N234CB	MA(1/20)	200	24	3.4	2.5
8	N234CB	MA(1/1, in Cl ₃ C ₆ H ₃)	200	12	4.5	7.8
9	N234CB	MA(1/10)	93	12	2.7	0.5
10	N234CB	MA(1/10)	200	14	4.8	6.3
11	N234CB	MA(1/4)	200	22	8.4	16.1
12	N234CB	MAA(1/4)	200	22	-	3.5 ^d
13	N234CB	SA(1/4)	200	22	-	2.5 ^d

Example 14-17: (TABLE 2) These samples were prepared by aqueous reaction of the selected treated carbons from TABLE 1 with nucleophiles. The resulting solid was then filtered, washed (water), and dried.

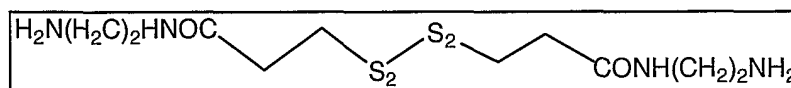
5
TABLE 2
Reactions of Maleic Anhydride-treated Carbon Black with
Nucleophiles. (*atomic % by XPS)

Ex. No.	Treated-C Ex No.	Nucleophile (mCO:mN)	Reaction Temp.	Reaction Time hr	%O*	%N*
14	11	H- (NHCH ₂ CH ₂ N H) _x -H (~0.3)	110°C	6	4.8	5.5
15	11	NH ₂ NH ₂ (0.5)	80	6	7.0	1.4
16	11	NH ₂ OH (1)	50	1	7.4	0.8
17	N/a	H ₂ O ₂	10	3	7.7	

Example 17 was prepared with a carbon black reacted with maleic anhydride under different conditions than examples 1-13. The material of Example 17 was made up to determine if peracid groups could be attached to the carbonyl functionalized carbon black. Example 17 illustrated that this was possible but the reaction temperature was desirably low so that the peracid doesn't decompose.

Examples 18: Preparation of Carbon Coupler

A coupler was prepared by reaction of 3-mercaptopropionic acid methyl ester with an excess of ethylene diamine at 30°C at for 1 hr to give a quantitative yield of the corresponding 1:1 mole ratio mercapto-amino amide (after removing unreacted ethylene diamine) by IR and elemental analysis, 20.3 S% (21.9% theory); 19.1 %N (18.89% theory). Two moles of this material was reacted with 3 moles of elemental sulfur at 100 C for 4 hr to give a 94.5% yield of a dark red glass, with IR and elemental analysis (32.7% S, 37.71% theory; 16.6% N, 15.63% theory) consistent with the corresponding amino amide polysulfide (EDA) of the structure:



Ex. 18

Example 19. CB/Malan pre-reacted with coupler (EDA) of Ex18. To MAA/CB from Ex 8 (410 g, corresponding to 18 g, 0.184 mole Malan), suspended in toluene, was added material from Ex 18 (31.3 g , 0.184 mole) in 20 ml of water

with stirring. The reaction was refluxed until no more water was removed (about 23 ml), and the solid washed with toluene and dried to give a solid, 431g,

Examples 20-26: Rubber formulations using various forms of carbon black are shown in TABLE 3. CB/no coupler is generally a control without maleic anhydride-or coupler (see Control for examples 20-26, Control for example 25, and Control for example 26). Multiple controls were used because the scorch time and/or the cure rate of the rubber compounds varied depending on the additional treatments to the carbon black. Therefore additional controls were run to reflect changes in the mixing procedures to compensate for different effective cure rates of the various rubber compounds. The Control for examples 20-26 is believed to have been an oxidized N234 with a slower cure rate. Pre-reacted C/MA/Ex 18 refers to the product of example 19 where maleic anhydride-treated carbon black was reacted with the coupler from Ex 18 in toluene. Since example 19 included 4 phr of coupler and 80 grams of carbon black it was added at 84 phr with no additional coupler. Pre-treat means that an aqueous solution of the coupler (Ex 18) was adsorbed onto the carbon black/maleic anhydride, followed by drying, prior to its addition to the rubber. Examples 21, 22, 23, and 25 show pre-treat with level of coupler going from 3 to 5 phr. In the "dry-mix" mode, the carbon black/maleic anhydride material was substituted for carbon black (@ 80 phr) and added directly, along with other coupler (4 phr of coupler), during rubber mixing (Ex 26). Example 24 uses CB/MAA (from Ex 8) without coupler. Addition of carbon black/maleic anhydride, coupler or pre-reacted coupler w/MA/CB (Ex 19) can be added in one portion, split over time, or over stages of the rubber mixing.

Rubber Composition for Examples 20-26:

	<u>Component</u>	<u>Level (PHR)</u>
25	Duradene 715 S-SBR	70
	Budene 1207 high cis BR	30
	N234 carbon black / MAA (or CB - control)	80
	Couplant (specified in Table 3)	0-5
30	Textracts 2202 aromatic oil	36
	ZnO – Stearic acid	3 – 2
	Sulfur – CBS accelerator	1.5 – 1.5
	Flexzone 7P antioxidant	1

Duradene 715 is a solution polymerized styrene-butadiene rubber from Firestone Polymers. Budene 1207 is a high cis-butadiene rubber from Goodyear. Couplant is specified in TABLE 3. CBS is N-cyclohexyl-2-benzothiazylsulfenamide. Flexzone 7P is N-(1,3-dimethyl butyl)-N'-phenyl-p-phenylenediamine from Uniroyal.

The additives are added at a phr level (parts by weight per hundred parts by weight rubber) according to the above alternatives to a carbon black/MAA filled rubber formulation intended for tires to improve the combination of rolling resistance and wet traction. Dynamic hysteretic behavior was measured and recorded in TABLE 3:

TABLE 3
Hysteretic behavior of maleic anhydride-treated carbon black with coupler.

Example No.	Carbon / Reactant	Coupler	tan delta 0° C	tan delta 60°C	Tan delta 0°/tan delta 60°	Mixing Method
control for items 20-26	N234	none	0.413	0.33	1.25	CB/no coupler
20	Example 19		0.347	0.24	1.45	pre-reacted, C/MA/Ex18 @ 84 phr
21	Example 8	Structure of Example 18 (5 phr)	0.319	0.229	1.39	pre-treat
22	Example 8	Structure of Example 18 (4 phr)	0.34	0.225	1.51	pre-treat
23	Example 8	Structure of Example 18 (3 phr)	0.339	0.248	1.37	pre-treat
24	Example 8	none	0.373	0.322	1.16	CB/MA no coupler
Control for item 25	N234	none	0.361	0.289	1.25	CB/no coupler
25	Example 2	Structure of Example 18 (4 phr)	0.299	0.211	1.42	pre-treat
Control for item 26	N234	none	0.372	0.274	1.36	CB/no coupler
26	Example 4	Structure of Example 18 (4 phr)	0.356	0.23	1.55	dry mix

Tan delta @60 °C is a measure of roll resistance; lower is better. Tan delta @ 0°C is a measure of wet skid resistance, higher is better. Tan delta 0 °/tan delta 60°C indicates by a higher number that gains in wet skid are being achieved without equivalent losses in rolling resistance or that reduction in rolling resistance is being achieved without an equivalent loss in wet skid resistance.

The results in Table 3 show that all of the treated carbon black materials used with coupler exhibit superior dynamic properties to non-treated controls, either in a "dry mix" or by pre-reacting the CB/MA with coupler.

Examples 27-32. Two grams of modified carbon black are placed in a burette with the carbon black resting on a small plug of glass wool. 50 g of a solution (deep greenish blue) of CuNaphthenate in Isopar G hydrocarbon solvent (200 ppm Cu) were slowly run through the carbon black absorbent at an approximate rate of 1.5 to 2 ml/min. Based on the amount of Cu removed the color of the solutions exiting the burette became lighter. The following visual scale was used to evaluate adsorbent performance: 5 = no color change (still same deep greenish blue), 0 = clear (no color visible in solution).

Example	Adsorbent	Visual Rating
27	Unmodified Carbon Black; 20-60 mesh	3
28	Carbon Black/malan (4:1)w; 20-60 mesh	0-1
29	Carbon Black/malan (4:1) w 60-100 mesh	0
30	(Carbon Black/malan (4:1)w)/NH ₂ OH; 20-60 mesh	0-1
31	Carbon Black/AMPS®* (4:1)w	4
32	Coal/malan (4:1)w	5

*AMPS is the trademark for a 2-acrylamido-2-methylpropane sulfonic acid monomer sold by the Lubrizol Corporation.

Examples 33-36. One gram of the modified carbon black was packed into a column and 100 g of a solution containing 1000 ppb Cu in Isopar G hydrocarbon solvent was allowed to flow through this column at a rate of ~ 7.5 g/min. The

resulting solution was then submitted for Cu analysis via a graphite furnace atomic adsorption analysis method.

Example	Adsorbent	Cu in ppb
33	Baseline Soln.	866 ppb
34	Carbon Black	< 10 ppb
35	Carbon Black/Malan (4:1)w	440 ppb
36	(Carbon Black/Malan)/NH ₂ OH	< 10 ppb

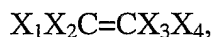
The results above indicate that maleic anhydride modified carbon black is an effective media (generally more effective than non-modified carbon black) for the removal of metals such as copper from hydrocarbon solvents. Example 30 illustrates that the maleic anhydride modified carbon black can be further reacted with a nucleophile which may improve the effectiveness of the carbon black as a filtration media.

Examples 33-36 illustrate that as the effectiveness of carbon black and maleic anhydride modified carbon black in removing the last 1000 ppb (1000 ppb = 1 ppm) of copper from a hydrocarbon solvent. In these particular examples the non-modified carbon black and the maleic anhydride modified carbon black further modified with a NH₂OH nucleophile performed better at removing this type of copper salt. The relative performance of these candidates is expected to vary as the amount of metal, type of metal, and type of counterion(s) are varied. In other experiments not reported herein the performance of the maleic anhydride modified carbon black was superior.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

What is claimed is:

- 5 1. A composition comprising the reaction product of (a) a solid form of
carbon and (b) a reactant of the structure



FORMULA I

or the structure



FORMULA II

and, optionally c) a continuous media, wherein X_1 , X_2 , X_3 and X_4 are independently selected from H, an alkyl of 1 to 4 carbons, or an electron withdrawing group, wherein at least one of X_1 , X_2 , X_3 and X_4 is a known electron withdrawing group, said electron withdrawing groups being characterized by having a $\sigma_p > 0$, where σ_p is the $\log(K'/K_0')$ where K' is the equilibrium constant for the ionization of a para substituted benzoic acid with the particular group and K_0' is the equilibrium constant for the ionization of benzoic acid in water at 25°C.

2. The composition of claim 1 wherein said solid form of carbon is other
20 than carbon black or coal.

3. The composition of claim 1 wherein said reactant is maleic anhydride or a diels alder adduct of a diene or polyene with maleic acid or anhydride, and optionally wherein said solid form of carbon is other than carbon black or coal..

4. The composition of claim 3 wherein the reaction conditions includes a
25 temperature of at least 200 °C for at least 2 hours.

5. The composition of claim 1, wherein said electron withdrawing group of said reactant of FORMULA I is selected from a carboxylic acid, anhydride of di or poly-carboxylic acids, acyl halide, ester, amide, nitrile, keto and aldehyde group, and optionally wherein said solid form of carbon is other than carbon black or coal..

30 6. The composition of claim 1 wherein said reactant is itaconic acid, glyoxylic acid, a glyoxylate ester, or a itaconic acid ester.

7. The composition of claim 1 wherein said solid form of carbon is graphite.
8. The composition of claim 7 wherein said reactant is maleic anhydride.
9. The composition of claim 8 wherein the reaction conditions includes a
5 temperature of at least 200°C for at least 2 hours.
10. The composition of claim 1 wherein said reaction product is further reacted with a nucleophile of the formula: R'-Nu, wherein R'-Nu contains one or more of any group known to react with said electron withdrawing groups which is at least one of X₁, X₂, X₃ and X₄, said nucleophilic groups including -NH₂, -NHR,
10 -NR₂, -OH, -SH, -SR, -PR₂, -OP(OR)₃, -NRNHR, -NRNR₂, -NROR, or -OOR, or any anionic form thereof, and wherein R and R' independently are hydrogen, a hydrocarbyl group, including a polyether or polyamine group, a cation-containing group, di, tri or polysulfide linkages or combinations thereof.
11. The composition of claim 10, wherein said solid form of carbon is
15 carbon black and said reactant is maleic anhydride.
12. The composition of claim 11 wherein said nucleophile is ethylene diamine.
13. The composition of claim 11 wherein said nucleophile is an ethylene polyamine.
- 20 14. The composition of claim 11 wherein said nucleophile is a polyamine of the formula H-[NH-CH₂-CH₂]_nNH₂, where n equals two or more.
15. The composition of claim 10 wherein said solid form of carbon comprises graphite, said reactant comprises maleic anhydride and said nucleophile comprises a hydroxyterminated polyether.
- 25 16. The composition of claim 10 wherein said solid form of carbon comprises graphite, said reactant comprises maleic anhydride and said nucleophile comprises potassium hydroxide.
17. The composition of claim 1 wherein said solid form of carbon comprises carbon fiber.
- 30 18. The composition of claim 17 wherein said reactant comprises maleic anhydride.

19. The composition of claim 17 wherein said reactant comprises methyl glyoxylate.
20. The composition of claim 17 wherein said reactant comprises acrylic or methacrylic acid.
- 5 21. The composition of claim 1 wherein said solid form of carbon comprises activated charcoal.
22. The composition of claim 21 wherein said reactant comprises maleic anhydride.
23. The composition of claim 21 wherein said reactant comprises acrylic, glyoxylic, itaconic, or methacrylic acid or their respective C₁-C₄ esters or partial esters.
- 10 24. The composition of claim 1 wherein said solid form of carbon comprises carbon nanotubes.
25. The composition of claim 24 wherein said reactant comprises maleic anhydride.
- 15 26. The composition of claim 10 wherein said solid form of carbon comprises graphite and said reactant comprises maleic anhydride.
27. The composition of claim 10 wherein said solid form of carbon comprises carbon fiber and said reactant is maleic anhydride.
- 20 28. The composition of claim 10 wherein said solid form of carbon comprises carbon fiber and said reactant comprises acrylic or methacrylic acid.
29. The composition of claim 1 wherein said solid form of carbon comprises activated charcoal and said reactant comprises maleic anhydride and optionally said reactant product is further reacted with a nucleophile of the formula R'-Nu, wherein R'Nu contains one or more of any group known to react with said electron withdrawing groups which is at least one of X₁, X₂, X₃, and X₄, said nucleophilic groups selected from -NH₂, -NHR, -NR₂, -OH, -SH, -SR, -PR₂, -OP(OR)₃, -NRNHR, -NRNR₂, -NROR, or -OOR, or any anionic form thereof, and wherein R and R' independently are hydrogen, a hydrocarbyl group, including a polyether or polyamine group, a cation-containing group, di, tri or polysulfide linkages or combinations thereof.
- 25 30

30. The composition of claim 1 wherein said solid form of carbon comprises activated carbon and said reactant is acrylic or methacrylic acid and optionally said reactant product is further reacted with a nucleophile of the formula R'-Nu, wherein R'Nu contains one or more of any group known to react with said
5 electron withdrawing groups which is at least one of X₁, X₂, X₃, and X₄, said nucleophilic groups selected from -NH₂, -NHR, -NR₂, -OH, -SH, -SR, -PR₂, -OP(OR)₃, -NRNHR, -NRNR₂, -NROR, or -OOR, or any anionic form thereof, and wherein R and R' independently are hydrogen, a hydrocarbyl group, including a polyether or polyamine group, a cation-containing group, di, tri or polysulfide
10 linkages or combinations thereof.

31. The composition of claim 10 wherein said solid form of carbon comprises carbon nanotubes and said reactant comprises maleic anhydride.

32. A waterborne ink or coating composition including the composition of claim 11.

15 33. A hydrocarbon based ink or coating composition including the composition of claim 11.

34. The composition of claim 10, where said solid form of carbon comprises graphite, said reactant comprises maleic anhydride and said nucleophile comprises ethylene diamine.

20 35. A hydrocarbon-based lubricating composition including the composition of claim .

36. A fiber-reinforced composite composition including the composition of claim 27.

25 37. A fiber-reinforced composite composition including the composition of claim 28.

38. A filtration media including the composition of claim 1 and optionally said reactant product is further reacted with a nucleophile of the formula R'-Nu, wherein R'Nu contains one or more of any group known to react with said electron withdrawing groups which is at least one of X₁, X₂, X₃, and X₄, said nucleophilic
30 groups selected from -NH₂, -NHR, -NR₂, -OH, -SH, -SR, -PR₂, -OP(OR)₃, -NRNHR, -NRNR₂, -NROR, or -OOR, or any anionic form thereof, and wherein R and R' independently are hydrogen, a hydrocarbyl group, including a polyether or

polyamine group, a cation-containing group, di, tri or polysulfide linkages or combinations thereof

39. A filtration media including the composition of claim 1 and optionally said reactant product is further reacted with a nucleophile of the formula R'-Nu, wherein R'Nu contains one or more of any group known to react with said electron withdrawing groups which is at least one of X₁, X₂, X₃, and X₄, said nucleophilic groups selected from -NH₂, -NHR, -NR₂, -OH, -SH, -SR, -PR₂, -OP(OR)₃, -NRNHR, -NRNR₂, -NROR, or -OOR, or any anionic form thereof, and wherein R and R' independently are hydrogen, a hydrocarbyl group, including a polyether or polyamine group, a cation-containing group, di, tri or polysulfide linkages or combinations thereof.

40. An oil-borne lubricating composition including the composition of claim 34.

41. A water-borne lubricating composition, including the composition of claim 15.

42. The composition of claim 10 wherein said solid form of carbon comprises anode coke, said reactant comprises maleic anhydride and said nucleophile comprises potassium hydroxide.

43. An electrode for aluminum production from Bauxite, including the composition of claim 42.

44. A fuel-cell electrode including the composition of claim 27.

45. A composition of claim 4 wherein said continuous media comprises polypropylene.

46. A composite for use in automotive body panels including the composition of claim 45.

47. A dispersion for electronic displays including the composition of claim 4.

48. A composition of claim 10 where said solid form of carbon comprises C₆₀ (buckminsterfullerene).

49. A composition according to claim 39, wherein said filtration media is used to purify an aqueous media, a hydrocarbon fuel, or a hydrocarbon lubricant.

50. A composition according to claim 49, wherein said filtration media is used to remove a cation and optionally its associated anion.

51. A composition according to claim 49, wherein said filtration media is used to remove a transition metal, optionally as a salt or complexed species.

5 52. A composition according to claim 51, wherein said transition metal has an atomic number between 21 and 29 inclusively.

53. A composition according to claim 52, wherein said transition metal is being removed from a fuel product.

10 54. A composition according to claim 49, wherein said filtration media is used to remove a transition metal from an aqueous media.

55. The composition of claims 3 or 9 wherein the carbon black and reactant are fed (as an aerosol) into a reactor heated to 200 to 500°C, more preferably 350 to 450°C, for a few seconds to several minutes resonance time.

15 [1] as defined in R. Alder, R. Baker and J. Brown, "Mechanism in Organic Chemistry", Wiley Interscience, 1971, London, p. 36 (Table 7).

[2] Reaction has occurred is indicated by the presence of peaks in the thermogravimetric analysis (TGA) of the adduct which are not due to free reactant or starting carbon.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/40060

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B31/00 C09C1/44 C09C1/46 C01B31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 203 814 B1 (OGATA NAOYA ET AL) 20 March 2001 (2001-03-20) column 10, line 28; example 12	1-4, 7-9, 17
X	column 17, line 15-55	5
Y	the whole document	1-55
X	DEYANOVA A S: "Electrically conducting polyethylene composition - contg. carbon black modified with maleic anhydride to increase elasticity and strength, used in sheets, pipes, vessels etc. mfr" DERWENT, XP002211229 abstract	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

27 April 2004

Date of mailing of the international search report

06/05/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Arnotte, E

INTERNATIONAL SEARCH REPORT

In ternational Application No
PCT/US 03/40060

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 134 261 A (DEGUSSA) 19 September 2001 (2001-09-19) paragraphs '0006!', '0007!', '0009!-'0016!; claims 1-6 ----	1-55
A	EP 0 896 986 A (MITSUBISHI CHEM CORP) 17 February 1999 (1999-02-17) paragraphs '0044!', '0045!', '0047!; claim 4 -----	1-55

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/40060

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6203814	B1	20-03-2001	AT 253193 T 15-11-2003
			AU 707522 B2 15-07-1999
			AU 4598096 A 26-06-1996
			CA 2207282 A1 13-06-1996
			DE 69532044 D1 04-12-2003
			EP 0796403 A1 24-09-1997
			JP 11502494 T 02-03-1999
			KR 263027 B1 01-08-2000
			US 2002086335 A1 04-07-2002
			WO 9618059 A1 13-06-1996
			US 6362011 B1 26-03-2002
			US 5866434 A 02-02-1999
EP 1134261	A	19-09-2001	DE 10012783 A1 18-10-2001
			EP 1134261 A2 19-09-2001
			JP 2001323185 A 20-11-2001
			US 2002096089 A1 25-07-2002
EP 0896986	A	17-02-1999	JP 10195331 A 28-07-1998
			JP 10212426 A 11-08-1998
			JP 10324818 A 08-12-1998
			DE 69721517 D1 05-06-2003
			DE 69721517 T2 18-03-2004
			EP 0896986 A1 17-02-1999
			US 6123759 A 26-09-2000
			CN 1230972 A ,B 06-10-1999
			WO 9830638 A1 16-07-1998
			JP 10237349 A 08-09-1998