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<p>(54) Title: CARBON BLACK PRODUCTS FOR COLORING MINERAL BINDERS</p> <p>(57) Abstract</p> <p>A mineral binder composition having incorporated therein a carbon black product comprising a carbon black having attached an organic group containing an ionic or an ionizable group.</p>

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DESCRIPTION

CARBON BLACK PRODUCTS FOR COLORING MINERAL BINDERS

Technical Field

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This invention relates to mineral binder systems which contain a carbon black product as a colorant.

Background Art

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Mineral binder systems used to form items such as concrete, cement, mortar and exterior plaster formulations are often colored to enhance their aesthetic appeal. Coloring can be accomplished either by applying a suitable coating to the exposed surfaces or by adding small amounts of one or more pigments to the mineral binder system to uniformly color the mix. Since surface coatings are subject to peeling, fading and weathering, the latter method of coloring is preferred. The pigment or pigments can be added either to the dry mineral mix, for example, in the case of concrete to the cement-sand mixture, or to the water used to set such a mix.

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Pigments which are suitable for coloring mineral binder systems which are exposed to outdoor conditions must 1) be alkali-resistant, 2) be lightfast, 3) be resistant to industrial atmospheres, and 4) weather at a comparable rate with the body in which it is mixed so that the appearance of the surface does not change substantially with time.

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In addition, for ease of application, the pigment should be relatively dust-free, and should easily disperse in the mix to attain its maximum coloring power.

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Black pigments are desirable colorants for use in mineral binder systems because a large variety of colors and color shades can be obtained by their use, either alone or in combination with other pigments. Black iron oxides are the most preferred black pigment, but carbon blacks are also used to a limited extent.

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While carbon blacks exhibit excellent coloring properties, alkali-resistance, lightfastness and chemical stability, they are not preferred in mineral binder systems exposed to outdoor weathering. Weathering studies show

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that the surface appearance of bodies containing carbon black undesirably changes as the weathering process progresses. When the system contains only carbon black as the coloring pigment, the surface fades. When the carbon black is used in combination with other colorants, the appearance of the other colorants become more pronounced. This change in carbon black-pigmented mineral systems has been attributed to the leaching out and washing away of the carbon black pigment particles, which are very small relative to the other ingredients. This has limited its use in systems exposed to outdoor weathering.

Additionally, depending on the physical form in which it is supplied, carbon black can be either very dusty or very difficult to disperse. The process used for incorporating the carbon black into a binder system depends on both the form in which the pigment is supplied and the processing equipment available to the user. As produced, carbon blacks are powdery materials with bulk densities ranging from about 0.02 to 0.1 g/cc and are termed fluffy blacks. Such blacks are very dusty. Because of their low densities and large surface areas, the fluffy products are cohesive, have very poor conveying properties and are therefore difficult to bulk handle. For this reason fluffy products have limited utility, and are generally supplied in bagged form. Fluffy blacks are, however, dispersible and can develop their full coloring potential by relatively simple grinding procedures. To improve the bulk handling properties of carbon blacks and reduce their dustiness, fluffy blacks are typically densified by various pelletizing procedures to attain bulk densities ranging from about 0.2 to 0.7 g/cc. For a given grade of carbon black, handling properties tend to improve with increasing degrees of densification. Dispersibility, on the other hand, is progressively degraded as the extent of densification is increased. Thus there is a tradeoff between improvement in bulk handling properties and degradation in dispersibility. Because of the advantages

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of increased cleanliness, however, pelletized carbon blacks are often used for introducing carbon blacks into mineral binder systems. In such cases, however, the extent of grinding or milling required to form a uniform, intimate mix will be greater than that which is employed with the fluffy form of the product.

Carbon black has been added to mineral binder systems in a variety of ways. It can be milled into the dry sand-cement mixture, for example, and then the requisite amount of water necessary for setting the mix can be added. Alternately, an aqueous dispersion of the carbon black, in all or part of the requisite volume of water necessary for setting the mix, can be uniformly blended into the sand-cement mixture. In either case, for full and uniform color development, the carbon black agglomerates must be broken down to yield primarily individual aggregates (the smallest dispersible units of carbon black). This is accomplished either by milling the dry mix or by predispersing, by milling, the carbon black in the aqueous medium. Since carbon blacks tend to be hydrophobic, surface active agents are often used to promote wetting. In addition, the presence of such an agent in the aqueous medium can enhance the dispersion process and aid dispersion stabilization.

Attempts have been made to improve both the weathering and dispersing properties of carbon blacks used to pigment mineral binder systems. For example, U.S. Patent No. 4,006,031 discloses that fluorine-containing wetting agents used with carbon blacks provides improved weathering properties to mineral binder systems. Others, as described in European Patent No. 50354, have used surface-active polymers which disperse the carbon black in the aqueous medium used to set the mineral binder system and then become inactive after drying. The benefits include better black dispersion, improved weathering resistance and decreased efflorescence. The disclosure of these patents is herein incorporated by reference.

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Nevertheless, even in these prior art processes, the carbon black, whether in fluffy or pelletized form, must be milled to attain the required degree of pigment dispersion. Thus, there remains a need for carbon blacks useful as colorants in mineral binder systems which can be used in pelletized form, yet easily disperse with low shear stirring and less readily wash out of the system during weathering.

Disclosure of the Invention

The present invention relates to a mineral binder composition having incorporated therein carbon black products comprising a carbon black having attached an organic group containing an ionic or an ionizable group. The carbon black products, when incorporated in a mineral binder system, offer superior weathering properties relative to conventional carbon black products.

Detailed Description of the Invention

The present invention relates to a mineral binder composition having incorporated therein carbon black products comprising a carbon black having attached an organic group containing an ionic or an ionizable group. The carbon black products, when incorporated in a mineral binder system, offer superior weathering properties relative to conventional carbon black products.

Suitable mineral binder systems include concrete, cement, mortar, and exterior plaster formulations. Other mineral binder systems are similarly useful herein. Any conventionally known additives for mineral binder systems may be incorporated in the mineral binder systems of the present invention.

The carbon black products may be prepared by reacting a carbon black with a diazonium salt in a liquid reaction medium to attach at least one organic group to the surface of the carbon black. The diazonium salt may contain the organic group to be attached to the carbon black.

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According to the invention, a diazonium salt is an organic compound having one or more diazonium groups. Preferred reaction media include water, any medium containing water, and any medium containing alcohol. Water is the most preferred medium. These carbon black products and various methods for their preparation are described in a U.S. patent application entitled "Reaction of Carbon Black with Diazonium Salts, Resultant Carbon Black Products and Their Uses," filed December 15, 1994 and incorporated herein by reference.

To prepare the above carbon black products, the diazonium salt need only be sufficiently stable to allow reaction with the carbon black. Thus, that reaction can be carried out with some diazonium salts otherwise considered to be unstable and subject to decomposition. Some decomposition processes may compete with the reaction between the carbon black and the diazonium salt and may reduce the total number of organic groups attached to the carbon black. Further, the reaction may be carried out at elevated temperatures where many diazonium salts may be susceptible to decomposition. Elevated temperatures may also advantageously increase the solubility of the diazonium salt in the reaction medium and improve its handling during the process. However, elevated temperatures may result in some loss of the diazonium salt due to other decomposition processes.

The carbon black can be reacted with a diazonium salt when present as a dilute, easily stirred, aqueous slurry, or preferably in the presence of the proper amount of water for carbon black pellet formation.

A preferred set of organic groups which may be attached to the carbon black are organic groups substituted with an ionic or an ionizable group as a functional group. An ionizable group is one which is capable of forming an ionic group in the medium of use. The ionic group may be an anionic group or a cationic group and the ionizable group may form an anion or a cation.

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5 Ionizable functional groups forming anions include, for example, acidic groups or salts of acidic groups. The organic groups, therefore, include groups derived from organic acids. Preferably, when it contains an ionizable group forming an anion, such an organic group has a) an aromatic group or a C1-C12 alkyl group and b) at least one acidic group having a pKa of less than 11, or at least one salt of an acidic group having a pKa of less than 11, or a mixture of at least one acidic group having a pKa of less than 11 and at least one salt of an acidic group having a pKa of less than 11. The pKa of the acidic group refers to the pKa of the organic group as a whole, not just the acidic substituent. More preferably, the pKa is less than 10 and most preferably less than 9. Preferably, the aromatic group or the alkyl group of the organic group is directly attached to the carbon black. The aromatic group may be further substituted or unsubstituted, for example, with alkyl groups. The C1-C12 alkyl group may be branched or unbranched and is preferably ethyl. More preferably, the organic group is a phenyl or a naphthyl group and the acidic group is a sulfonic acid group, a sulfinic acid group, a phosphonic acid group, or a carboxylic acid group. Examples include -COOH, -SO₃H and -PO₃H₂ and their salts, for example -COONa, -COOK, -COO-NR₄⁺, -SO₃Na, -HPO₃Na, -SO₃-NR₄⁺, and PO₃Na₂, where R is an alkyl or phenyl group. Particularly preferred ionizable substituents are -COOH and -SO₃H and their sodium and potassium salts.

10 Most preferably, the organic group is a substituted or unsubstituted sulfophenyl group or a salt thereof; a substituted or unsubstituted (polysulfo)phenyl group or a salt thereof; a substituted or unsubstituted sulfonaphthyl group or a salt thereof; or a substituted or unsubstituted (polysulfo)naphthyl group or a salt thereof. A preferred substituted sulfophenyl group is hydroxysulfophenyl group or a salt thereof.

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Specific organic groups having an ionizable functional group forming an anion are p-sulfophenyl, 4-hydroxy-3-sulfophenyl, and 2-sulfoethyl.

5 Quaternary ammonium groups ($-NR_3^+$) and quaternary
phosphonium groups ($-PR_3^+$) represent examples of cationic
groups and can be attached to the same organic groups as
discussed above for the ionizable groups which form anions.
Preferably, the organic group contains an aromatic group
such as a phenyl or a naphthyl group and a quaternary
10 ammonium or a quaternary phosphonium group. The aromatic
group is preferably directly attached to the carbon black.
Quaternized cyclic amines, and quaternized aromatic amines,
can also be used as the organic group. Thus, N-substituted
pyridinium compounds, such as N-methyl-pyridyl, can be used
15 in this regard.

An advantage of the carbon black products having an
attached organic group substituted with an ionic or an
ionizable group is that the carbon black products may have
increased water dispersibility relative to the
20 corresponding untreated carbon black. In general, water
dispersibility of the carbon black products increases with
the number of organic groups attached to the carbon black
having an ionizable group or the number of ionizable groups
attached to a given organic group. Thus, increasing the
25 number of ionizable groups associated with the carbon black
products should increase their water dispersibility and
permits control of the water dispersibility to a desired
level.

When water dispersible carbon black products of the
30 present invention are prepared, it is preferred that the
ionic or ionizable groups be ionized in the reaction
medium. The resulting product solution or slurry may be
used as is or diluted prior to use. The carbon black
products may be pelletized, preferably by a conventional
35 wet process, pin pelletizing operation.

The carbon black products may be dried by techniques
used for conventional carbon blacks. These techniques

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include, but are not limited to, drying in ovens and rotary kilns. Overdrying, however, may cause a loss in the degree of water dispersibility. In the event that the carbon black products above do not disperse in the aqueous vehicle as readily as desired, the carbon black products may be dispersed using conventionally known techniques such as milling or grinding.

The carbon black products may be incorporated either in solid form or as a preformed liquid dispersion. The preferred addition of carbon black product is of an amount less than or equal to 5% by weight of the mineral binder. These mineral binder systems have improved weathering properties as shown in the Examples below.

Experimental

The carbon blacks used were characterized with respect to their structure using n-dibutyl phthalate absorption, DBP, using ASTM D 2414. Surface area was characterized by adsorption of cetyltrimethylammonium bromide, CTAB, using ASTM D 3765.

Pin Pelletizing

Pin Pelletizing was accomplished using both a pilot scale continuous and a laboratory scale batch pin pelletizer. The batch unit consisted of an 18-cm (7-inch) diameter by 17-cm long cylinder containing a central shaft fitted with a plurality of pins extending almost to the cylinder wall. The shaft was rotated at about 500 RPM during the pelletizing operation. The continuous unit consisted of a 25.5-cm (10-inch) diameter by 155-cm (61-inch) long cylindrical body fitted with a rotor running along its axis. The rotor, fitted with about 120 1.27-cm (0.5-inch) diameter pins extending almost to the walls of the unit, was rotated at a specified RPM to form pellets.

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Measurement Of Aqueous Residue

This procedure was used to obtain a measure of product dispersibility. The carbon black (5g) was vigorously shaken with 45 g of water for 5 minutes. The resulting slurry was poured through a 325 mesh (44 micron) screen and rinsed with water until the washings were colorless. The dried weight of residue on the screen was determined and expressed as a percentage of the carbon black used in the test.

Product Dispersibility

A measure of product dispersibility was obtained by dispersing the various blacks in an aqueous medium having a pH of about 10 under low shear conditions by means of a magnetic stirrer for 30 minutes. For the control, unmodified blacks, cetyl trimethyl ammonium bromide, a surfactant known to stabilize carbon black dispersions, was added to the medium. No surfactant was used in the case of the carbon black products. The slurry optical density, (OD)_{low shear}, was determined at a wavelength of 550 nm. Thereafter, the slurry was sonified (to reflect intense milling) and the slurry optical density, (OD)_{sonified}, determined. The percent change in optical density before and after sonification, $\Delta(\text{OD}) = 100[(\text{OD})_{\text{sonified}} - (\text{OD})_{\text{low shear}}] / (\text{OD})_{\text{sonified}}$ was calculated. A large percent change in this value indicates poor low shear dispersibility for the dispersion conditions employed.

Colored Concrete Formulation

Concrete was colored with a mixture of carbon black and natural red iron oxide pigment. Two procedures were used to introduce the black into the concrete mix. All quantities cited are in parts by weight. In the first procedure, 90 parts of red iron oxide and 6 parts of carbon black or the carbon black product were thoroughly mixed in a pestle and mortar until additional mixing gave no change in color. 1.4 parts of the mixed color was then mixed

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with 60 parts of sand and 14 parts of cement by spatula. Thereafter, about 10 parts water was added and the mixture was worked by spatula to form a paste. The paste was cast into channels (8.5 cm long x 1 cm wide x 1.5 cm deep) and allowed to slowly dry under ambient conditions. In the second procedure, all quantities used to form the colored concrete were identical with those in the first procedure. In this case, however, the carbon black or carbon black product, 0.0875 parts, was added to the water used to set the concrete. None was added to the red iron oxide. In all cases the blacks were dispersed in the water under low shear dispersion conditions by stirring for 30 minutes using a magnetic stirrer.

The reflectance spectrum of the dry, colored concrete was determined. The reflectance values were used to compute the International Commission on Illumination CIE 1976 L* a* and b* values. L* represents the lightness coordinate running from 0 for a pure black to 100 for a pure white; a* represents the red-green coordinate with its value becoming larger as the degree of redness increases; b* represents the yellow-blue coordinate with its value becoming larger as the degree of yellowness increases.

Weathering

Weathering was simulated by contacting the concrete for 30 seconds with undiluted SURE CLEAN® 600 detergent supplied by ProSoco, Inc., Kansas City, Kansas. The product is a blend of organic and inorganic acids combined with wetting agents and is normally diluted with water and employed to clean new masonry. The concrete was then washed with copious amounts of distilled water, dried and then its surface reflectance redetermined. The neat, undiluted product vigorously attacks the alkaline concrete so that some of the surface layers are washed away. Changes in L*, a* and b* (ΔL^* , Δa^* and Δb^*) before and after treatment give a measure of preferential leaching.

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ExamplesExample 1

This example illustrates the preparation of a carbon black product having an attached p-C₆H₄SO₃⁻ group. A fluffy carbon black (200 g) having a CTAB surface area of 350 m²/g and a DBP of 120 cc/100 g carbon and 42.4 g sulfanilic acid were placed in the batch pin pelletizer. After mixing for 40 seconds by means of the rotor, a solution of 20.7 g of sodium nitrite, NaNO₂, in 150 g water was added to the pelletizer. 4-Sulfobenzene diazonium hydroxide inner salt is formed in situ which reacts with the carbon black. After mixing for 45 seconds by means of the rotor, the carbon black product was transformed into pellets. These were dried in an oven at 120°C. The pelletized product had handling properties at least comparable to conventionally pelletized carbon blacks and was dispersible. Using the aqueous residue test, it had a 325 mesh residue of 0.6% compared to 97% for the untreated, fluffy black.

A sample of the product was subjected to Soxhlet extraction overnight with tetrahydrofuran. Analysis of the extracted sample showed that it contained 3.47% sulfur, compared to 0.5% sulfur for the untreated fluffy carbon black. Therefore, the carbon black product has 0.93 mmol/g of attached p-C₆H₄SO₃⁻ groups.

Example 2

This example illustrates the preparation of a carbon black product having an attached p-C₆H₄CO₂⁻ group. Stock solutions A and B were formed as follows:

Stock solution A: 19 g of concentrated hydrochloric acid (about 36% HCl) and 20 g water

Stock solution B: 8.0 g NaNO₂ and 39.2 g water

The stock solutions were chilled to 5°C. To 10.3 g of stock solution A 1.58 g of anthranilic acid (o-amino benzoic acid) was added. Thereafter, 10.5 g of stock solution B was slowly added while ensuring that the temperature did not exceed 10°C. The resulting solution,

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kept in an ice bath, was stirred for 15 minutes. It was then added to a slurry of 20 g of the fluffy black used in Example 1 in 350 ml water. The resulting slurry was stirred for 15 minutes and then filtered. The filter cake was washed twice with water and then dried in an oven at 110°C. While this product was not pelletized, the dried cake had a density which was comparable to that of the pelletized product and had much better handling properties than the fluffy precursor.

Dispersibility

The dispersibilities of the products of Examples 1 and 2 were evaluated using the optical density procedure. The controls employed were the untreated, fluffy black and its conventional dry drum pelletized counterpart. The percent change in optical density is presented in Table 1.

Table 1
Percent Change In Slurry Optical Densities On Sonification

Product	Δ (OD), %
Example 1	26.8
Example 2	91.4
Fluffy Control	92.4
Dry Drum Pelletized Control	100

The Δ (OD) values in the table show that the products of Example 1 and Example 2 are more dispersible than the conventional dry drum pelletized product under low shear dispersion conditions. In spite of their much larger bulk densities, the dispersibility of the product of Example 2 is comparable to, and that of Example 1 substantially superior to, that of the undensified, fluffy black.

Evaluation Of Concrete Colored With Carbon Black Samples

The products of Examples 1 and 2 as well as the fluffy and dry pelletized control blacks were used to form colored

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concrete using the pestle and mortar mixing process, Procedure I, and the low shear aqueous dispersion process, Procedure II. The L*, a* and b* values found are given in Table 2.

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Table 2
Color Values Attained In Concrete

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Products	Procedure I			Procedure II		
	L*	a*	b*	L*	a*	b*
Example 1	23.20	2.57	3.63	21.18	1.97	3.00
Example 2	21.71	2.01	2.41	28.76	4.95	5.75
15 Fluffy	27.53	2.99	3.54	40.85	1.86	2.69
Dry Pelletized	27.47	3.67	4.22	31.82	3.90	3.68

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The results in Table 2 show that when the carbon products of this invention are incorporated into concrete by Procedure I, the pigmented concretes have darker colors, as shown by their smaller L* values, than the either dry pelletized or fluffy carbon blacks. With procedure II, where the blacks are dispersed under low shear conditions in water, the product of Example 1, being the most dispersible (see Table 1), gives the darkest color. The product of Example 2 forms the next darkest color. Surprisingly, the fluffy black, which is more dispersible than the dry drum pelletized product, gave a pigmented concrete with the lightest surface color. This is attributed to segregation of the pigment away from the surface layers because, as will be shown, a much darker color is obtained when the surface is washed with the SURE CLEAN® detergent.

Weathering Of Colored Concrete Samples

5 Simulated weathering was conducted by washing the surfaces of the samples characterized in Table 2 with the SURE CLEAN® 600 detergent and water. The acidic detergent, in all cases, attacked the surfaces of the samples. The L*, a* and b* values of the washed surfaces are presented in Table 3. The aggressive washing procedure employed, in all cases, resulted in some change in the appearance of the surface. The change in the appearance, however, was lowest for the carbon products of the present invention.

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Table 3
Color Values Of Washed Concrete

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Products	Procedure I			Procedure II		
	L*	a*	b*	L*	a*	b*
Example 1	22.10	3.06	6.21	21.00	2.46	5.58
Example 2	20.69	2.52	5.24	25.49	5.22	8.11
Fluffy	24.33	3.66	6.29	28.22	2.20	5.43
Dry Pelletized	26.31	4.34	7.64	24.22	4.95	7.63

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25 The changes in color values on washing are shown in Table 4.

Table 4
Change In Color On Washing

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Products	Procedure I			Procedure II		
	ΔL^*	Δa^*	Δb^*	ΔL^*	Δa^*	Δb^*
Example 1	1.10	-0.49	-2.58	0.18	-0.49	-2.58
Example 2	1.02	-0.51	-2.83	3.27	-0.27	-2.36
Fluffy	3.20	-0.67	-2.75	12.63	-0.34	-2.74
Dry Pelletized	1.16	-0.67	-3.42	7.60	-1.05	-3.95

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5 For each procedure used to form the concrete, the magnitude
of the ΔL^* value is smallest for the carbons products of
the present invention. Apart from the sample formed with
the fluffy black using Procedure II where some color
segregation occurred and the change in ΔL^* is very large,
10 the magnitude of the Δa^* values are smallest for the
products of the present invention. Finally, the values of
 Δb^* are reasonably comparable for all the samples.
Accordingly, the present results show that the color
changes are smallest with the black products of the present
invention.

15 Example 3

The present example shows that the carbon black
products can be formed in a continuous pelletizing
operation. A fluffy carbon black having a surface area of
133 m²/g and a DBP of 190 cc/100 g carbon was introduced
20 into a continuously operating pin pelletizer at a rate of
100 parts by weight per hour. Simultaneously, a 30%
solution of sodium nitrite and a suspension containing
5.43% concentrated nitric acid, 8.72% sulfanilic acid and
85.9% water were introduced into the pelletizer. The
25 sodium nitrite solution and the suspension were introduced
at rates of 16 and 112 parts by weight per hour,
respectively. 4-Sulfobenzendiazonium hydroxide inner salt
was generated *in situ* and reacted with the carbon black in
the pelletizer. The material exiting the pelletizer is the
30 treated black, in pelletized form, and was dried at 125 °C.
These materials may also be used in the mineral binder
systems to obtain superior weathering properties.

35 Additional embodiments of the invention will be
apparent to those skilled in the art from consideration of
the specification and practice of the invention disclosed
herein. The specification and examples are intended to be
exemplary only.

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The claimed invention is:

1. A mineral binder composition having incorporated therein a carbon black product comprising a carbon black having attached an organic group containing an ionic or an ionizable group.

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2. A composition of claim 1 wherein the carbon black product is a water dispersible carbon black product.

3. A composition of claim 2 wherein the carbon black product is dispersed in the mineral binder composition by means of low shear stirring or mixing.

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4. A composition of claim 1 wherein the carbon black product is present in an amount of less than or equal to 5% by weight of the mineral binder.

5. A composition of claim 1 wherein the carbon black product is in pelletized form.

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6. A composition of claim 1 wherein the mineral binder is selected from concrete, cement, mortar, and plaster.

7. A composition of claim 1 wherein the ionic or the ionizable group is a carboxylic acid or a salt thereof.

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8. A composition of claim 1 wherein the ionic or the ionizable group is a sulfonic acid or a salt thereof.

9. A composition of claim 1 wherein the organic group is a sulfophenyl group or a salt thereof.

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10. A composition of claim 1 wherein the organic group is p-sulfophenyl or a salt thereof.

11. A composition of claim 1 wherein the organic group is a carboxyphenyl group or a salt thereof.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/16281

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09C1/56 C04B14/36 C04B33/14

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 6 C09C C04B

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,24 26 266 (DEGUSSA) 11 December 1975 & US,A,4 006 031 (...) cited in the application ---	
A	WO,A,92 13983 (CNRS) 20 August 1992 see page 13, paragraph 1-2 ---	1
A	FR,A,1 331 889 (BAYER) 5 July 1963 see page 1, paragraph 1; claim 1 ---	1
A	FR,E,72 775 (J. B. A. DONNET & SOCIÉTÉ D'ÉTUDE DES INDUSTRIES DU PÉTROLE (...)) 28 April 1960 see page 5, right column, last paragraph; claim 1 -----	1

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Information on patent family members

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