

[54] SURFACE MODIFIED PIGMENTS

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[21] Appl. No.: 26,380

[22] Filed: Apr. 2, 1979

Related U.S. Patent Documents

Reissue of:

[64] Patent No.: 3,290,165

Issued: Dec. 6, 1966

Appl. No.: 269,695

Filed: Apr. 1, 1963

U.S. Applications:

[63] Continuation-in-part of Ser. No. 189,321, Apr. 23, 1962, abandoned.

[51] Int. Cl.<sup>3</sup> ..... C09C 3/12

[52] U.S. Cl. .... 106/308 N

[58] Field of Search ..... 106/308 B, 308 N, 308 O; 428/405; 260/42.15

[56] References Cited

U.S. PATENT DOCUMENTS

2,742,378	4/1956	Te Grotenhuis .....	106/308 N
2,832,754	4/1958	Jex et al. ....	260/46.5
3,015,569	1/1962	Frieser .....	106/308 N
3,029,209	4/1962	Ferrigno .....	260/2.5
3,150,109	9/1964	Ferrigno .....	260/2.5
3,158,519	11/1964	Shannon et al. ....	106/308 N
3,168,389	2/1965	Eilerman .....	106/308 N

FOREIGN PATENT DOCUMENTS

863412	3/1961	United Kingdom .....	106/308 N
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OTHER PUBLICATIONS

Jellinek et al., Silane Finishes for Fibrous Glass, Presented Before the Society of Plastic Industries, Chicago, Ill., Feb. 5-7, 1957.

Primary Examiner—James Poer

Attorney, Agent, or Firm—Robert L. Price; Harold H. Flanders

[57] ABSTRACT

*Finely divided particulate inorganic pigment is surface modified with from about 1% to about 15% of an amino organosilane, particularly gamma-aminopropyltriethoxy silane. Thermosetting resins incorporating such modified inorganic pigments exhibit improved physical properties.*

8 Claims, No Drawings



## SURFACE MODIFIED PIGMENTS

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

This application is a reissue of U.S. Pat. No. 3,290,165, Ser. No. 269,695 filed April 1, 1963, which is a continuation-in-part of applicant's copending application Ser. No. 189,321, filed April 23, 1962, entitled "Surface Modified Pigments," and now abandoned.

This invention relates to finely divided particulate inorganic pigments modified with amino organosilanes and the process for their production.

When inorganic pigments are modified with the silanes according to this invention, the properties imparted to them are such that they can advantageously be used as fillers for thermosetting resins such as polyurethanes, epoxy polymers, melamine polymers, phenolic polymers, ureaformaldehyde polymers, unsaturated polyesters, as well as other polymers and elastomers including polyethylenes, polypropylenes, polystyrenes, saturated polyesters, polyamides, polyvinyl compounds, polyisoprenes, polybutadienes, polystyrenebutadienes, and the like.

The modified pigments can also be advantageously used as fillers for paper, paints, varnishes, inks, and paper coating compositions.

By the use of these modified finely divided particulate inorganic pigments, improved physical properties are imparted to the vehicles into which they are incorporated.

Inorganic pigments modified with amino organosilanes have affinity for direct dyes and are useful for imparting various colors to the vehicles.

An object of this invention is to provide modified pigments especially useful as fillers.

Another object of this invention is to provide modified pigments which are dyeable with direct dyes and are useful as color-imparting fillers.

A further object of this invention is to provide modified pigments which can be used as fillers in applications where they had heretofore been unsatisfactory.

A still further object of the invention is to provide cross-linkable fillers capable of imparting improved abrasion resistance among other improved properties to elastomers.

Other objects and advantages will be apparent from the following specification.

I am aware of extensive efforts in the prior art to improve properties of filler pigments by modification with organosilanes. Hydrocarbon silane modifications of pigments do impart improved dispersions in organic vehicles but such modifications do not normally increase reinforcement in vinyl addition polymers unless the hydrocarbon silane carries specific types of unsaturation which serves to promote a more tenacious bridge between the filler and the vehicle. In any case, all these prior art modified pigments are rendered hydrophobic by modification with either saturated or unsaturated hydrocarbon silanes and, furthermore, such silane modified pigments are not valuable reinforcing fillers in saturated thermosetting resins.

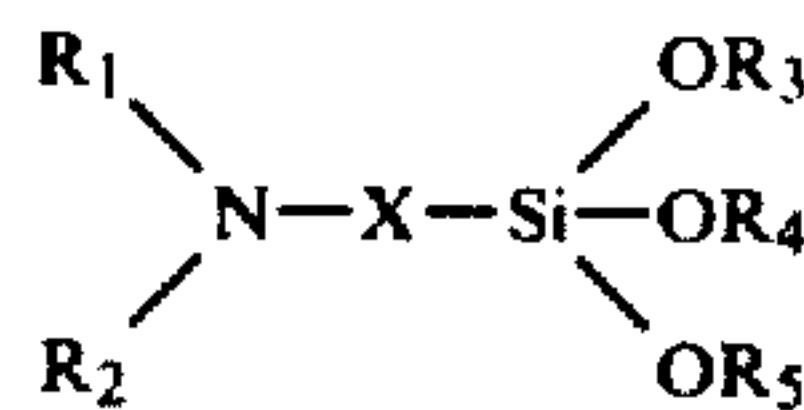
I have discovered that modification of filler pigments with saturated amino organosilanes improves reinforcement in a wide variety of vinyl addition as well as ther-

mosetting polymers in that a strong chemical bridge between filler pigment and polymer results. Bridging is accomplished through the amino modified surface of the pigments. Surprisingly, amino organosilane modification improves reinforcement in both vinyl addition and thermosetting polymers, whereas unsaturated organosilane fillers are generally only effective in vinyl addition polymers where unsaturation is present. Another important advantage of amino organosilane modified fillers is that they are usually hydrophilic whereas prior art silane modified fillers are hydrophobic.

The modified pigments of this invention can be prepared by dissolving the desired amount of amino organosilane in a suitable solvent, adding the pigment and heating until the reaction is complete. The amount of modifier added depends upon the particular pigment being modified and the use for which it is intended. Generally up to about 15% by weight of the modifier is sufficient for most purposes.

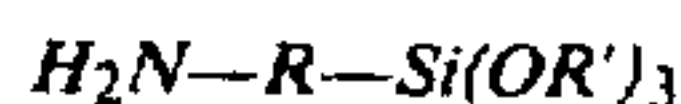
A particularly useful process of modifying pigments according to this invention involves spray drying pigment slurries having one or more of the amino organosilanes dispersed therein. The spray drying process effects a uniform distribution of the modifier on the pigment and virtually instantaneously cures the modifier on the pigment.

The compounds used to modify the pigments can be depicted by the formula:



wherein  $R_1$  is hydrogen, alkyl, aryl, cycloalkyl, or alkylaryl;  $R_2$  is hydrogen, alkyl, aryl, cycloalkyl or alkylaryl;  $R_3$  is hydrogen, lower alkyl, aryl, lower alkylaryl, or lower arylalkyl;  $R_4$  is hydrogen, lower alkyl, aryl, lower alkylaryl or lower arylalkyl;  $R_5$  is hydrogen, lower alkyl, aryl, lower alkylaryl or lower arylalkyl; and  $X$  is alkylene, arylene, alkylarylene, arylalkylene, cycloalkylene having secondary and/or tertiary nitrogen present in the chain, and/or primary, secondary, and/or tertiary nitrogen pendant from the chain. Some of these amino organosilanes are disclosed along with methods for their preparation in U.S. Pat. Nos. 2,832,754; 2,930,809; 3,007,957; and 3,020,302. Commercially available amino organosilanes include "A-1100" (gamma aminopropyltriethoxysilane) and "Y-2967" (an amino silane which is a modified gamma aminopropyltriethoxysilane) sold by Union Carbide Corporation, N.Y., N.Y., and "Z-6020" (a diamino functional silane) sold by Dow Corning Corporation, Midland, Michigan.

Preferred compounds to modify the pigments are amino organosilanes of the formula:



wherein  $R$  is selected from the group consisting of phenylene, lower alkyl substituted phenylene, lower alkoxy substituted phenylene, and lower alkylene.  $R'$  is monovalent hydrocarbon group free of aliphatic unsaturation selected from the group consisting of lower alkyl, aryl, lower alkaryl and lower aralkyl, wherein  $R'$  can represent the same or different groups.

Pigments advantageously modified in the practice of this invention are finely divided particulate inorganic pigments such as, for example, inorganic compounds of



silicon, including hydrated or anhydrous silicas, calcium silicates, magnesium silicates, calcium-magnesium silicates, barium silicates, aluminum silicates, sodium-alumino-silicates, calcium-alumino-silicates, calcium-sodium alumino silicates; clays such as kaolins which include dickite, kaolinite and nacrite, halloysite, montmorillonites including sodium and magnesium bentonites, synthetic or natural zeolites; various metal oxides and carbonates such as zinc oxide, alumina, titania or magnesia, calcium carbonate; and various non-white pigments like carbon blacks, zinc sulfide, ferric oxide and the like.

All the above fillers are available on a commercial scale and include the following, all of which are finely divided, particulate substances.

Zeolex®, very finely divided precipitated sodium alumino silicate pigments of submicron particle size and disclosed in U.S. Pat. Nos. 2,739,073 and 2,848,346.

Zerosil®, very finely divided precipitated hydrated silicas of submicron particle size and disclosed in co-pending U.S. Pat. applications Ser. No. 144,168 filed Oct. 10, 1961, and 149,964 filed Nov. 3, 1961.

Suprex®, an air floated kaolin clay with platelike particles of which 87-92% are minus 2 microns.

Aromex®, intermediate super abrasion furnace carbon blacks.

Essex®, semi-reinforcing furnace blacks.

Silene EF®, a precipitated hydrated calcium silicate of very fine particle size.

Hi-Sil®, a precipitated hydrated silica of very fine particle size.

Celite®, a diatomaceous earth which is principally a hydrated silica.

Alumina C®, a hydrated aluminum oxide of small particle size.

Kadox®, a zinc oxide filler.

Titanox®, a pigment grade commercial titanium dioxide.

Cab-O-Sil®, a very finely divided anhydrous silica.

Ludox®, a precipitated silica of very fine particle size.

The following examples illustrate typical methods by which various pigments are surface modified in accordance with this invention.

#### Example 1

8 grams of gamma aminopropyltriethoxysilane (A-1100) was dissolved in 3.3 liters of benzene in a 5-liter round bottom flask. 400 grams of carbon black (ISAF) was added and the resulting mixture was refluxed 2 hours. The resulting product contained 2% of the modifier based on the weight of the carbon black.

#### Example 2

"Suprex" was modified with 1.0% by weight with gamma aminopropyltriethoxysilane by adding the appropriate amount of the modifier using water as a solvent and then adding the clay and refluxing for 2½ hours. The products were recovered and dried. The example was repeated with 2.0% and 3.0% gamma aminopropyltriethoxysilane.

#### Example 3

"Zeolex 23" was modified with 1% by weight with gamma aminopropyltriethoxysilane by adding the "Zeolex" to a benzene solution of the modifier and refluxing for 2½ hours. The product was recovered and dried.

#### Example 4

"Suprex" was modified with 1.0% of "Z-6020" by adding 3.33 pounds "Z-6020" to 667 pounds of water while under agitation. 333 pounds of "Suprex" was slowly added to the solution while continuing the stirring until a homogeneous clay slip resulted. The clay slip was then spray dried in a 7-foot conical spray dryer operated at an inlet temperature of 600° F. and an outlet temperature of 250° F. A finely pulverized, chemically modified clay product was obtained. The example was repeated to produce 2.0% and 3.0% modifications of the "Suprex."

#### Example 5

Example 4 was repeated using "Y-2967" instead of "Z-6020."

#### Example 6

Example 4 was repeated using "A-1100" instead of "Z-6020."

#### Example 7

"Suprex" was modified with 1% of gamma aminopropyltriethoxysilane by adding 10 grams gamma aminopropyltriethoxysilane to 3.5 liters benzene, then adding 1 kilogram "Suprex" clay and refluxing for 3 hours. The modified clay was recovered and dried. This example was repeated using 2% and 3% instead of 1% gamma aminopropyltriethoxysilane.

#### Example 8

Example 7 was repeated using "Z-6020" in place of gamma aminopropyltriethoxysilane.

#### Example 9

Example 7 was repeated using "Y-2967" in place of gamma aminopropyltriethoxysilane.

The above examples illustrate the facility with which various inorganic pigments are modified with amino organosilanes.

The examples were repeated using each of the pigments named herein to produce modified pigments having properties similar to those discussed below.

While only three modifiers are exemplified, this is done for convenience since all those disclosed herein have been used for the purpose and come within the scope of this invention.

The physical properties of the various pigments disclosed herein are significantly altered by modification with the group of silanes disclosed herein. For example, when kaolin clay is so modified, a dramatic change in its properties is apparent. Where, before, the clay lacked significant affinity for direct dyes, it is modified by the process of this invention to be readily dyeable with direct dyes. The modified kaolin clays can be used as a filler for polyurethanes where, before modification, it was unusable since it prevented a cure of the polymer. This is illustrated in Table I in which the following formation was employed:

	Parts
Vibrathane 5003 <sup>1</sup>	100
Stearic acid	0.25
Di-Cup 40C <sup>2</sup>	5



-continued

Clay	Parts
	60

<sup>1</sup>A polyurethane produced by Naugatuck Chemical Division of U.S. Rubber Company.

<sup>2</sup>A polymerizing cross-linking agent produced by Hercules Powder Company.

The compounds were mixed on a 6-inch by 12-inch laboratory mill and cured for 30 minutes at 307° F., except for the NBS abrasion test where the cure was for 60 minutes at 307° F.

TABLE I

	Control	Suprex	Example 2		
			Suprex plus 1% Modifier	Suprex plus 2% Modifier	Suprex plus 3% Modifier
Parts filler/100 parts polymer	None	60	60	60	60
Tensile, p.s.i.	5,240	No cure	3,680	3,770	3,840
Stress, 300%, p.s.i.	830	No cure	2,070	3,190	—
Elongation, percent	500	No cure	470	425	265
Shore A Hardness g	56	No cure	71	71	75
NBS Abrasion, percent of standard	129	No cure	122	172	202

The results illustrate the improved properties of modified kaolin clay filled polyurethane over both the compound filled with unmodified kaolin and the unfilled compound. Note, for example, the increase in abrasion resistance with increased modification of kaolin. It is also apparent from the data that unmodified kaolin is unsatisfactory as a filler for polyurethanes since the polymer did not cure. The use of modified kaolin clay not only improves the properties of the polyurethane but also decreases the raw material cost since the filler is much less expensive than the polymer.

When modified carbon black is used as the filler in a rubber recipe, good results compared to unmodified black are achieved with a 2% by weight modification using gamma aminopropyltriethoxysilane. The results listed in Table III are based upon tests in the following recipe.

	Parts/100 RHC
Smoked sheet	100.0
ISAF carbon black	45.0
Zinc oxide	3.0

Stearic acid	3.0
Pine tar	3.0
Age rite HP <sup>1</sup>	1.0
NOBS special <sup>2</sup>	0.35
Sulfur	2.75
Total	158.10

<sup>1</sup>An antioxidant containing phenyl-beta-naphthylamine and N,N'-diphenyl-para-phenylenediamine.

<sup>2</sup>Accelerator containing N-oxydiethylene benzothiazol-2-sulfenamide.

The batches were mixed on a Banbury using speed #1, ram pressure of 30 p.s.i., and a starting temperature

TABLE II

MODIFIED SUPREX CLAYS IN VIBRATHANE 5003								
Physical Properties	Minutes Cured at 305° F.	Unfilled Control	Suprex Filled Control	Example 2		Example 4 1% Z-6020 Water	Example 8 1% Z-6020 Benzene	Example 9 1% Y-2967 Benzene
				1% Modifier Water	2% Modifier Water			
200% Modulus	30	430	1,270	1,340	2,900	—	2,900	1,710
	60	500	1,310	1,530	2,990	2,890	1,710	—
	75	510	1,330	1,480	2,820	—	2,860	1,840
300% Modulus	30	830	1,570	2,070	3,190	—	3,270	2,060
	60	1,050	1,640	2,220	3,340	3,330	3,270	2,090
	75	1,040	1,630	2,520	3,200	—	3,240	2,170
Tensile Strength	30	5,240	4,340	3,680	3,770	2,960	3,470	4,040
	60	4,890	3,850	3,920	3,490	3,620	3,290	3,610
	75	5,320	3,640	3,560	3,510	—	3,240	3,950
Elongation	30	500	570	470	425	190	365	560
	60	440	525	450	335	360	315	500
	75	450	505	440	370	—	300	510
Hardness, Shore A	30	56	72	71	71	75	75	70
	60	59	74	73	73	76	76	71
	75	59	74	73	73	13	76	71
Crescent Tear	30	65	285	280	238	225	235	303
	60	68	270	230	243	205	193	220
	75	73	243	231	225	—	193	225
NBS Abrasion Index, Percent	60	74.8	63.6	77.2	109.5	143.5	131.4	68.2
	75	80.3	62.2	87.4	137.0	105.5	152.1	81.5
Hardness, Shore A, NBS Specimens	60	55	71	72	75	76	76	71
	75	56	73	73	75	76	76	72
NBS Abrasion (Gum = 100%)	60	100	85	103	147	192	176	91
	75	107	83	117	183	141	204	109
Compression Set "B" 22 hrs./158° F.	60	5.5	34.0	17.5	11.3	10.1	12.0	25.0
	75	5.1	36.7	16.5	12.0	9.5	11.0	23.9
Mooney Viscosity, ML 4'/212° F.	—	44	60	65	65	83	65	64
Mooney Scorch, MS/265° F.	—	23	26	20	16	12.5	18	23

Table II demonstrates dramatic improvements in properties of polyurethane filled with amino organosilane modified clays.

of 125° F.; the final batch mix was on a 6-inch by 12-inch mill and the inlet water temperature was 158° F.



The compound was cured for 70 minutes at 275° F., then tested. The results are listed in Table III.

TABLE III

Pigment	Percent Modifier	Modulus, p.s.i.	Tensile, p.s.i.	Abrasion, Huber-Williams
ISAF Carbon Black Control.	None	1,780	4,590	100.0
ISAF Carbon Black	1	1,970	4,720	107.9

<sup>1</sup>2.0% gamma aminopropyltriethoxysilane.

This data indicates that when carbon black is modified with controlled amounts of modifier, the properties which it imparts to rubber are improved in respect to modulus, tensile, and abrasion resistance.

When modified Zeolex is used as a filler for rubber compounds, it imparts to the rubber improved properties of modulus, tensile strength, tear resistance and abrasion resistance when compared to these same properties in rubber filled with unmodified Zeolex. The results in Table IV are based upon the following recipe:

Parts/100 RHC	
GRS 1502 <sup>1</sup>	100.0
Pliolite S6B <sup>2</sup>	20.0
Zinc oxide	3.0
Stearic acid	2.0
Cumar MH 2 $\frac{1}{2}$ <sup>3</sup>	7.5
Zeolex 23	66.5
Santocure <sup>4</sup>	2.0
DOTG <sup>5</sup>	1.0
Sulfur	2.5
Total	204.5

<sup>1</sup>Emulsion copolymer of 23.5% styrene and 76.5% butadiene.

<sup>2</sup>A styrene-butadiene copolymer of high styrene content.

<sup>3</sup>Para-cumarene-indene resin.

<sup>4</sup>n-Cyclohexyl-2-benzothiazole sulfenamide accelerator.

<sup>5</sup>Di-ortho-tolylguanidine.

The recipe was mixed on a Banbury mixer at speed #1, ram pressure of 30 p.s.i., and at a starting temperature of 125° F. The final batch was mixed on a 6-inch by 12-inch mill with a water inlet temperature of 158° F. The compound was cured at 292° F., then tested. The results are shown in Table IV.

TABLE IV

Cure Minutes	200% Modulus	300% Modulus	400% Modulus	Tensile	Elongation	
PIGMENT-ZEOLEX 23 UNMODIFIED-CONTROL						
5	80	—	—	80	280	
10	80	—	—	80	280	
15	470	650	860	1,300	605	
20	720	1,000	1,350	1,640	460	
30	750	1,060	1,450	1,560	420	
PIGMENT-ZEOLEX 23 MODIFIED WITH 10% GAMMA AMINO-PROPYLTRIETHOXYSILANE						
5	690	1,010	1,340	1,970	580	
10	910	1,300	1,710	2,480	550	
15	1,010	1,400	1,820	2,360	510	
20	1,070	1,480	1,920	2,280	470	
30	1,090	1,480	1,940	2,360	480	
		Abrasion Index <sup>1</sup>			Shore Hardness	
Pigment		10'	15'	20'	10'	15' 20'
Zeolex 23 Control		2	41.5	47.5	60	72 77
Modified Zeolex 23		61.7	63.0	62.3	76	76 77
		Tear Resistance, Avg.				
Pigment		5'		10'	15'	20'
Zeolex 23 Control		37.5		38.5	174	160

TABLE IV-continued

Modified Zeolex 23	216.5	193.5	195	187.5
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<sup>1</sup>Percent of NBS Standard sample.

<sup>2</sup>Not cured.

The results indicate that Zeolex 23 modified with gamma aminopropyltriethoxysilane, when compared with unmodified Zeolex 23 used as a filler for rubber, is faster curing, has increased modulus, increased tensile strength, and improved tear resistance and abrasion resistance.

It should also be noted that physical and "wet" electrical properties of filled resin systems can be significantly improved by treating the fillers in accordance with this invention.

I have found that in addition to the concepts disclosed above, the properties of the modified pigments are affected by the solvent used in their preparation.

The properties of carbon blacks, clays and silicates modified in aqueous systems, such as disclosed in Example 2, vary markedly from the properties of these same pigments modified in nonaqueous systems as disclosed in Examples 1 and 3.

In order to demonstrate these differences, regular Suprex clay, Suprex clay of Example 2, and Suprex clay modified in nonaqueous solvent according to the teachings of Example 7 were used in producing rubber compounds using the following recipe.

Parts by weight	
Smoked sheet <sup>1</sup>	100
Clay (as specified in Table V)	104
Zinc oxide	5
Sulfur	3
Captax	1
Stearic acid	4

<sup>1</sup>Natural rubber.

The compounds were mixed on a 6-inch by 12-inch laboratory mill and then cured at 260° F. to produce 30-, 45-, and 60-minute cures of each.

Table V below compares the abrasion index and the 200% modulus level of each of the test materials.

TABLE V

Clay	Abrasion Index, Percent			200% Modulus p.s.i.		
	30'	45'	60'	30'	45'	60'
Suprex Control	55.0	55.9	53.7	760	960	990
Suprex 3% Modifier (Benzene)	72.8	68.6	65.2	2,000	2,070	2,170
Suprex 3% Modifier (Water)	84.6	85.5	70.7	1,740	1,970	1,990

The results as set forth in Table V clearly indicate that clays modified in accordance with the invention impart superior properties to rubber compounds when used as a filler therein. These results also demonstrate that the clays modified in an aqueous system give a higher abrasion resistance and a lower modulus than clays modified in a nonaqueous system.

While natural rubber was used in the recipes tested in Table V, these tests were also conducted with similar results from recipes using SBR, polyurethanes and polybutadiene.

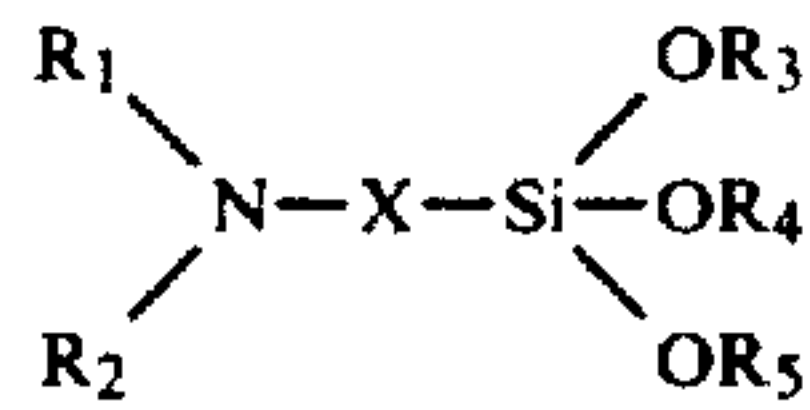
The foregoing is illustrative only and additional modifications may be made without departing from the



substance of the invention as defined in the appended claims.

I claim:

1. A filler comprising a finely divided particulate inorganic pigment surface selected from the group consisting of synthetic silicas, silicates, metal oxides, calcium carbonates, zinc sulfides, and carbon blacks, said pigment surface having been modified by treatment with from about 1% to 15%, based on the weight of the dry pigment, of an amino organosilane of the formula



wherein  $R_1$  is selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl, and alkylaryl,  $R_2$  is selected from the group consisting of hydrogen, alkyl, aryl, cycloalkyl and alkylaryl,  $R_3$  is selected from the group consisting of hydrogen, lower alkyl, aryl, lower alkylaryl and lower arylalkyl,  $R_4$  is selected from the group consisting of hydrogen, lower alkyl, aryl, lower alkylaryl and lower arylalkyl,  $R_5$  is selected from the group consisting of hydrogen, lower alkyl, aryl, lower alkylaryl, and lower arylalkyl,  $X$  is selected from the group consisting of alkylene, arylene, alkylarylene, arylalkylene, cycloalkylene containing secondary amino nitrogen, and cycloalkylene containing tertiary amino nitrogen, the modification of said pigment surface by said organosilane comprising spray drying slurries of said pigment having one or more of the amino organosilanes dispersed therein.

[2. A compound as in claim 1 wherein the finely divided particulate filler is selected from the group consisting of synthetic silicas, silicates, metal oxides, calcium carbonates, zinc sulfides, and carbon blacks.]

3. A compound as in claim 1 wherein the amino organosilane is gamma aminopropyltriethoxysilane.

4. A compound as in claim 1 wherein the amino organosilane is a diamino functional silane.

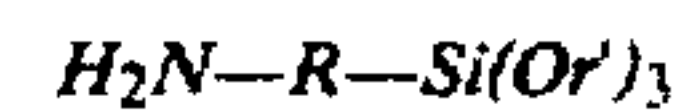
5. Finely divided particulate hydrated silica, surface modified with from about 1% to 15% by weight based upon the weight of the silica of gamma aminopropyltriethoxysilane.

6. Finely divided particulate sodium alumino silicate pigment, surface modified with from about 1% to 15% by weight, based upon the weight of the pigment, of gamma aminopropyltriethoxysilane.

7. Finely divided particulate carbon black, surface modified with from about 1% to 15% by weight, based upon the weight of the carbon black, of gamma aminopropyltriethoxysilane.

8. Finely divided particulate kaolin clay, surface modified with from about 1% to 15% by weight, based upon the weight of the kaolin clay, of gamma aminopropyltriethoxysilane.

9. A filler comprising a finely divided particulate inorganic pigment surface selected from the group consisting of synthetic silicas, silicates, metal oxides, calcium carbonates, zinc sulfides, and carbon blacks, said pigment surface having been modified by treatment with from about 1% to 15%, based on the weight of the dry pigment, of an amino organosilane of the formula



wherein  $R$  is selected from the group consisting of phenylene lower alkyl substituted phenylene, lower alkoxy substituted phenylene, and lower alkylene,  $R'$  is a monovalent hydrocarbon group free of aliphatic unsaturation selected from the group consisting of lower alkyl, aryl, lower alkaryl and lower aralkyl, wherein  $R'$  can represent the same or different groups.

\* \* \* \* \*

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**UNITED STATES PATENT AND TRADEMARK OFFICE  
CERTIFICATE OF CORRECTION**

PATENT NO. : Re. 30,450  
DATED : December 16, 1980  
INVENTOR(S) : Joseph Iannicelli

It is certified that error appears in the above—identified patent and that said Letters Patent is hereby corrected as shown below:

Column 2, line 38, "loer" should be -- lower --.

Column 3, line 19, "Zerosil" should be -- Zeosil --.

Column 4, line 62, "formation" should be -- formulation --.

Column 5, Table II, in seventh column opposite "Hardness Shore A, 75 min.", the figure "13" should be omitted.

Column 6, line 31, "benzothlazol" should be -- benzothiazol --.

Column 7, line 37, "Para-cumarene-indene" should be -- Para-cumarone-indene --.

Column 7, line 64, in second column opposite "Zeolex 23 Control" the figure "2" should be footnote -- (2) --.

Column 10, line 32, following "lene", insert a comma -- , --.

**Signed and Sealed this**

***Fourteenth Day of April 1981***

**[SEAL]**

***Attest:***

**RENE D. TEGTMEYER**

***Attesting Officer***

***Acting Commissioner of Patents and Trademarks***