PATENT SPECIFICATION

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(54) CURABLE COMPOSITIONS COMPRISING AQUEOUS SOLUTIONS OF WATER-SOLUBLE SILICATES AND WATER-SOLUBLE LATENT INSOLUBILIZING AGENTS

(71) We, PPG INDUSTRIES, INC., a corporation organized and existing under the laws of the State of Pennsylvania, United States of America, of One Gateway Center, Pittsburgh, State of Pennsylvania, 15222, United States of America, (Assignees of JOHN EDWARD BLASKO, WILLIAM GEORGE BOBERSKI AND JEROME ALLAN SEINER), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a curable composition composed substantially of inorganic constituents. More particularly, the present invention relates to curable compositions comprising aqueous solutions of water-soluble silicates and water-soluble latent insolubilizing agents.

During the past several years, environmental pollution concerns have led those active in the coatings, castings, and moldings industries to investigate various compositions in which organic solvents derived from petroleum have been eliminated or at least substantially reduced in quantity. Thus, compositions such as water-based compositions and high solids compositions have been extensively investigated. Even more recently the petroleum embargo and the resultant high cost and scarcity of petroleum by-products has increased interest in the investigation of compositions which are composed substantially of inorganic constituents.

A number of water-soluble silicate compounds are known in the art. Such compounds include sodium silicate, potassium silicate, lithium silicate and quaternary ammonium silicates which readily dissolve in water to form solutions therewith. Inasmuch as the pH of these solutions is normally higher than about 10.5, the silica will remain soluble therein. However, when these water-soluble silicates are blended with insolubilizing agents (i.e. crosslinkers) quite often the resultant solution is unstable. Thus, for example, the combination of water-soluble silicates with metal oxides of the form MO such as cadmium oxide, copper oxide, calcium oxide, lead oxide and the like has produced unstable systems in that these materials ordinarily cause precipitation of insoluble hydroxides or silicates of these oxides. In addition to problems of composition stability, films formed from water-soluble silicates and water-soluble insolubilizing agents have in the past proven to be extremely sensitive to water. Thus, such compositions have heretofore been deficient in wet abrasion resistance.

Accordingly, as will be apparent, a curable composition containing a water-soluble inorganic silicate and a water-soluble latent insolubilizing agent which exhibits excellent stability and produces cured products having excellent durability, stain resistance, resistance to heat and flame and water-resistance as well as other desirable properties is of considerable advantage.

The present invention relates to curable compositions having the above-mentioned advantages. The curable compositions are prepared by forming aqueous solutions of water-soluble silicates and water-soluble latent insolubilizing agents formed from a metal ion selected from the group consisting of Al^{+++}, Fe^{+++}, Cr^{+++}

and Sn^{++} and a ligand selected from the group consisting of ethylenediaminetetraacetate, diethylenetriaminepentaacetate, N-(hydroxyethyl)-ethylenediaminetriacetate, nitrilotriacetate and 1,3-propanediaminetetraacetate, or alkali metal or quaternary ammonium zincates, aluminates or borates. The compositions preferably have dispersed therein certain inorganic pigments, preferably TiO_2.

The compositions of the invention have a number of advantageous properties. Thus, the curable compositions herein have excellent stability. Further, the curable compositions can be cured by removal of water from the compositions which can be accomplished either by drying the compositions in air at ambient temperature or by the use of moderate baking temperatures. Finally, these curable compositions form cured products having excellent durability, stain resistance, resistance to heat and flame and water resistance. Good water resistance is indicated by coatings of the cured composition passing a wet-abrasion resistance test.

This invention is concerned with the discovery of curable compositions which are composed substantially of inorganic constituents. The curable compositions of the invention comprise aqueous solutions of water-soluble silicates and water-soluble latent insolubilizing agents.

Water-soluble silicates which may be employed in the compositions herein include sodium silicate, potassium silicate, lithium silicate, quaternary ammonium and the like. A preferred water-soluble silicate is potassium silicate.

One group of water-soluble latent insolubilizing agents which are employed in the compositions herein are those formed from metal ions selected from the group consisting of Al^{+++}, Fe^{+++}, Cr^{+++} and Sn^{++} and ligands (i.e., complexing agents) selected from the group consisting of ethylenediaminetetraacetate, diethylenetriaminepentaacetate, N-(hydroxyethyl)ethylenediaminetetraacetate, nitrilotriacetate and 1,3-propanediaminetraacetate.

Illustrative examples of such latent insolubilizing agents are compounds such as sodium ethylenediaminetetraacetato aluminate (III), sodium ethylenediaminetetraacetato ferrate (III), sodium ethylenediaminetetraacetato chromate (III), sodium ethylenediaminetetraacetato stannate (II) and the like.

Another group of water-soluble metallate latent insolubilizers which are employed in the compositions of the invention are alkali metal or quaternary ammonium zincates, aluminates and borates.

Illustrative of such metallate latent insolubilizers which can be employed are alkali metal zincate, aluminate and borate compounds such as, for example, lithium zincate, potassium zincate and sodium zincate; lithium aluminate, potassium aluminate and sodium aluminate; and lithium borate, potassium metaborate and sodium tetraborate. The term "borate" as used in connection with the alkali metal borates is intended to include orthoborates, pyroborates, metaborates and more complex borate ions.

While not wishing to be bound by any particular theory, it should be noted at this time that while the above compounds exist prior to their addition to the alkaline environment (e.g., pH of 10.5—12.5) of the aqueous solution containing the water soluble alkali silicate, it is possible that these compounds may not be present in the alkaline environment in the exact compositional form indicated.

The amount of latent insolubilizers included in the compositions herein can vary considerably depending upon desired properties. However, in general, the amount of latent insolubilizer employed is an amount sufficient to enhance wet abrasion and water resistance of the cured composition but which is insufficient to cause package instability in the uncured composition. A stable package is defined as a package which, when aged for 24 hours at 160°F has not formed an irreversable gel and which still provides a wet abrasion resistant coating. Preferred compositions are stable at 160°F for at least about two weeks. Wet abrasion, resistance is evaluated by soaking a cured, coated glass panel, drawn with a 3 mil drawbar, in water (temperature 70°F + to 5°F) for one hour and then rubbing the surface of the cured coating with a water soaked cloth and determining the number of back and forth finger rubs (double finger rubs) needed to abrade the coating surface and expose the substrate. 50 finger rubs are considered as the minimum acceptable abrasion resistance. Preferred coatings pass 100 double finger rubs, while the most preferred coatings pass 200 double finger rubs without complete abrasion. Amounts of latent insolubilizers ranging from 0.1 percent to 5.0 percent, preferably 0.25 percent to 2.0 percent by weight, based upon the combined weight of the water-soluble silicate and latent insolubilizer are employed.

The reaction between the water-soluble silicate (i.e., alkali silicate) and latent insolubilizer is not known with certitude, however, it is theorized that ions associate with the silicate thereby maintaining the composition in a stable configuration. However, upon drying (e.g., air drying or baking) the equilibria shift and the associated ion then crosslinks the silicate to form an insoluble silicate composition having excellent properties such as stain resistance, flame and heat resistance and water resistance.

In addition to the water-soluble silicate and metallate latent insolubilizer, the curable compositions of the invention preferably contain an inorganic pigment selected from titanium dioxide; zirconium dioxide; alumina, preferably hydrated alumina or tin oxide. The amount of this pigment should be an amount which provides at least about a 2.5% pigment volume concentration (PVC). The maximum of this pigment which can be employed is that amount which together with other "inert solid" i.e. solids other than the solids contributed by the soluble silicate-latent insolubilizer binder, is the "critical PVC" i.e. the concentration of material above which the amount of binder present is insufficient to provide a coherent, abrasion resistant film. Obviously this upper limit will vary with the precise materials employed, but is readily determinable by minimal experimentation. In most cases investigated this upper limit appears to be at a PVC about 70.

In the preferred embodiment the inorganic pigment is titanium dioxide, preferrably having a surface coating of Al_2O_3/SiO_2. Such coated titanium dioxide pigments are known in the art.

In addition to the above essential components the curable compositions of the invention may contain other additives usually employed in coating compositions including dyes, coloring pigments, inorganic fillers or extenders, antioxidants, flow control agents, and surfactants. As known in the art many of these coating adjuvants may be partially or completely organic in nature, if desired.

Another unusual aspect of the compositions of the invention is the discovery that the addition of phosphate type surfactants to these compositions improves adhesion without impairing water resistance. Thus, for example, phosphate type surfactants or wetting agents such as potassium tripolyphosphate, sodium tripolyphosphate and organo phosphates such as PK—90, available commercially from the Dexter Chemical Corporation, may be employed.

In addition it is often advantageous to include in the composition a thickener. Of particular value are water-soluble thickeners which are solubilized through carboxyl groups. Illustrative of such materials are sodium polyacrylate, potassium polymethacrylate, sodium salts of styrene maleic anhydride copolymers, sodium carboxymethyl cellulose, and potassium polyacrylate copolymers. Also suitable are inorganic thickeners such as clays.

As mentioned above, the curable compositions of the invention can be employed in various applications such as for coatings, castings or moldings. The compositions are particularly useful in coatings over a variety of substrates such as wood, metals, glass, wallboard and the like.

The curable compositions herein can be applied by a conventional method, including brushing, dipping, rolling, flow coating, roll coating, and spraying. Conventional spray techniques and equipment can be utilized.

The curable compositions of the invention may be cured by baking at moderate or elevated temperatures if desired. However, one advantageous property of these curable compositions is that they can be cured by drying them in air at ambient temperature without the use of heat. As will be evident, ambient temperature curable compositions are of considerable advantage in that they provide for significant energy savings in comparison to compositions which require elevated temperatures for curing.

The following Examples are submitted for the purpose of further illustrating the nature of the present invention and should not be construed as a limitation on the scope thereof. All parts and percentages in the Examples and throughout the specification are by weight unless otherwise indicated.

All the compositions of the invention disclosed in the Examples have better wet abrasion resistance than if they did not contain the latent insolubilizing agents as may be seen from the comparative data which is present in some of the Examples. Further, all the compositions of the invention disclosed in the Examples possess package stability.

The following Examples illustrate the preparation of pigmented compositions.

Example 1.

A curable coating composition was prepared using conventional paint mixing techniques and equipment by admixing 231.3 grams of an aqueous potassium silicate solution having an SiO_2:K_2O ratio of 3.3:1 and a solids content of 38.8 percent by weight (available commercially under the designation Kasil No. 6 from Philadelphia Quartz Company), 1.35 grams of sodium aluminate (available in dry form from Reynolds Company), 181.3 grams of water, 105.0 grams of titanium dioxide, 72.5 grams of mica, 10.0 grams of Attagel 40 (a magnesium aluminum silicate thixotropic agent available from Engelhard Minerals Company), 2.2 grams of Foamaster G (an antifoaming agent available from Nopco Chemical Company) and 3.6 grams of PK—90 solution (a solution consisting of 0.6 grams of PK—90, an organic phosphate available from Dexter Chemical Company, and 3.0 grams of water).

The curable composition resulting from the above procedure was drawn down on several sets of glass panels using a 3 mil Bird Bar. One set of coated glass panels was cured by air drying at ambient temperature for one day, a second set of coated glass panels was cured by air drying at ambient temperature for 3 days and a third set of coating glass panels was cured by air drying at ambient temperature for 6 days.

The cured coatings were then evaluated for wet abrasion resistance by soaking the coated glass panels in water (temperature 70°F. ± 5°F.) for one hour and then rubbing the surface of the cured coating with a water soaked cloth. The wet abrasion resistance was evaluated by determining the number of back and forth finger rubs (recorded as double finger rubs) needed to abrade the coating surface and expose the substrate.

In this Example, the coating cured by air drying at ambient temperature for one day abraded after 2 double finger rubs while the coating cured by air drying at ambient temperature for 3 to 6 days respectively did not abrade after 200 double finger rubs. A similar composition except that it contained no metal complex, failed this test at 1 and 16 double finger rubs in two trials after 13 days of air drying.

Example 2.

A curable coating composition was prepared using conventional paint mixing techniques and equipment by admixing 231.3 grams of an aqueous potassium silicate solution having an SiO_2:K_2O ratio of 3.3:1 and a solids content of 38.8 percent by weight available commercially under the designation Kasil No. 6 from Philadelphia Quartz Company; 2.70 grams of sodium aluminate, 181.3 grams of water, 105.0 grams of titanium dioxide, 72.5 grams of mica, 10.0 grams of Attagel 40, 2.2 grams of Foamaster G, an antifoaming agent available from Nopco Chemical Company, and 3.6 grams of the PK—90 solution of Example 1.

The curable composition resulting from the above procedure was drawn down on glass panels, cured and evaluated for wet abrasion resistance as in Example 1.

In this Example, the coating cured by air drying at ambient temperature for one day abraded after three double finger rubs while the same coating cured by air-drying at ambient temperature for 3 and 6 days respectively did not abrade after 200 double finger rubs.

Examples 3—6.

Curable coating compositions were prepared by admixing the following ingredients:

Ingredients	Ex. No.	Parts by Weight (Grams) 3	4	5*	6
Aqueous potassium silicate solution of Example 1		231.50	231.30	231.30	231.30
Water		184.60	183.00	179.20	185.00
Sodium aluminate		1.35	2.70	5.40	1.00
Foamaster G(1)		2.20	2.20	2.20	2.20
Titanium dioxide		105.00	105.00	105.00	105.00
Mica		72.50	72.50	72.50	72.50
Sodium carboxymethyl cellulose		12.50	12.50	12.50	12.50
Attagel 40(2)		10.00	10.00	10.00	10.00
PK—90 solution(3)		3.60	3.60	3.60	3.60

(1) Defoamer available from Nopco Chemical Company.

(2) A magnesium aluminum silicate thixotropic agent available from Engelhard Minerals Company.

(3) A solution consisting of 0.6 gram of PK—90, an organic phosphate available from Dexter Chemical Company, and 3.0 grams of water.

* Composition gelled due to high level of sodium aluminate.

The compositions of Examples 3, 4 and 6 were drawn down on several sets of glass panels using a 3-mill Bird Bar. One set of coated glass panels was cured by air-drying at ambient temperature for 3 days, a second set of coated glass panels was cured by air-drying at ambient temperature for 7 days and a third set of coated glass panels was cured by air-drying at ambient temperature for 10 days.

The cured coatings were then evaluated for wet abrasion resistance using the procedure set forth in Examples 1 and 2. Test results are shown in Table I.

Table I.

Cured Coating of Example No.	Cure Conditions	Wet Abrasion (No. Double Finger Rubs) Cure Time (Days) 3 Days	7 Days	10 Days
3	Air dry at ambient temp.	1	4	85
4	”	1	151	>200
6	”	1	5	107

Examples 7—9.

Coating compositions were prepared by admixing the following ingredients:

Ingredients	Ex. No.	Parts by Weight (Grams) 7	8	9
Aqueous potassium silicate solution of Example 1		231.30	231.30	231.30
Water		184.00	184.00	184.00
Sodium aluminate			0.65	1.00
Foamaster G		2.20	2.20	2.20
Titanium dioxide		105.00	105.00	105.00
Mica		72.50	72.50	72.50
Sodium carboxymethyl cellulose		12.50	12.50	12.50
Attagel 40		10.00	10.00	10.00
PK—90 solution of Examples 3—6		3.60	3.60	3.60

The above compositions were drawn down on glass panels using a 3-mil Bird Bar, cured by air drying at ambient temperature for 3 days and the cured coatings then evaluated for wet abrasion resistance using the procedure set forth in Examples 1—6.

The coating of Example 7 which contains no crosslinker abraded after 4 double finger rubs while the cured coatings of Examples 8 and 9 did not abrade after 200 double finger rubs.

Example 10.

A curable coating composition was prepared by admixing the following ingredients:

Ingredients	Parts by Weight (Grams)
Aqueous sodium silicate solution(1)	231.0
Sodium aluminate	0.5
H_2O	168.0
Surfactant mixture(2)	14.1
Foamaster VL(3)	2.2
Mica	72.5
Sodium carboxymethyl cellulose	12.5
TiO_2	94.7
Red iron oxide (Fe_2O_3)	12.2
Attagel 40	10.0

(1) A solution having an SiO_2:Na_2O ratio of 3.22:1 and a solids content of 38.3 percent by weight available from Diamond Shamrock.

(2) A surfactant mixture consisting of 150.0 grams of H_2O, 80.0 grams of antarox BL 240 (a non-ionic surfactant available from GAF Corporation), 12.0 grams of the PK—90 solution of Example 1, and 40.0 grams of a 50 percent aqueous solution of potassium tripolyphosphate.

(3) A defoamer available from Nopco Chemical Company.

The above composition was drawn down on a glass panel using a 3 mil Bird Bar and the coated panel was cured by air-drying at ambient temperature for 10 days.

The cured coating was then evaluated for wet abrasion resistance using the procedure set forth in Examples 1—9.

The cured coating of this example passed 100 double finger rubs before abrading.

The following examples illustrate the preparation of unpigmented (i.e., clear) compositions.

Examples 11—14.

Coating compositions were prepared by admixing the following ingredients:

		Parts by Weight			
Ingredients	Ex. No.	11	12	13	14
		(Control)			
Aqueous potassium silicate solution*		308.0	308.0	308.0	308.0
Water		40.0	40.0	40.0	40.0
Sodium aluminate		—	0.5	1.0	2.0

* A solution having an SiO_2:K_2O ratio of 3.93:1 and a solids content of 29.1 percent by weight, available from Philadelphia Quartz Company.

The above compositions were drawn down on glass panels using a 3-mil Bird Bar and cured by drying in air at ambient temperature for 7 days. The coated panels were then soaked in tap water for ten (10) minutes and evaluated for wet abrasion resistance using the procedure in Examples 1—10. Test results are shown in Table II.

Table II.

Cured Coating of Example No.	Cured Conditions	Wet Abrasion (No. of Double Finger Rubs)
11	7 days air dry at ambient temperature	2
12	”	60
13	”	85
14	”	100+

Examples 15—21.

Coating compositions were prepared by formulating the following ingredients:

Ingredients Ex. No.:	Parts by weight						
	15	16	17	18	19	20	21
Aqueous potassium,[1] silicate solution	308.6	308.6	308.6	308.6	308.6	308.6	308.6
Sodium Aluminate solution[2]	100.5	100.5	100.5	100.5	100.5	100.5	100.5
Organic phosphate[3] wetting agent	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Antifoam agent[4]	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Water	13.2	31.8	44.5	53.6	60.7	66.3	68.6
Mica (Micromica)	72.5	48.2	31.7	19.6	11.4	3.1	0
TiO_2 (CLNC grade)	105.0	69.8	45.9	28.4	15.0	4.4	0
Magnesium aluminum silicate (Attagel 40)	10.0	6.6	4.4	2.7	1.4	0.4	0
Pigment Volume Concentrations	55%	45%	35%	25%	15%	5%	0

(1) as in Examples 11—14

(2) 0.5 parts sodium aluminate/100 parts water

(3) Strodex PK—90

(4) Foammaster VL

The above compositions were drawn down on two series of glass panels using a 3-mil Bird Bar. One series of panels was air dried at ambient temperature for 3 days, the other series of panels was dried at ambient temperature for 5 days. The cured coatings were evaluated for wet abrasion resistance using the procedure set forth in Examples 1—8.

Table III.

Cured Coating of Example No.	Curing Conditions	Wet Abrasion (No. of double finger rubs)
15	3 days at ambient temperature	>200 chip broke off at 20
16	3 days at ambient temperature	10—20 broke off in pieces
17	3 days at ambient temperature	abraided away at 200 — a blistered area failed at 10
18	3 days at ambient temperature	abraided away at 200 — a blistered area failed at 10
19	3 days at ambient temperature	>200 in thin areas — about 20 in puddled area
20	3 days at ambient temperature	at 200 in thin areas — about 5 in puddled area
21	3 days at ambient temperature	failed at about 10
15—21	5 days at ambient temperature	all passed 200

Examples 22—27.

Coating compositions were prepared by formulating the following ingredients:

Ingredients	Ex. No.	Parts By Weight 22	23	24	25	26	27
potassium silicate solution (as Ex. 11—14)		400	343	314	294	265	245
sodium aluminate		0.65	0.58	0.51	0.48	0.43	0.40
organic phosphate wetting agent (Strodex PK—90)		0.6	0.6	0.6	0.6	0.6	0.6
antifoam agent (Foamaster VL)		3.2	3.2	3.2	3.2	3.2	3.2
TiO_2		65.7	71.1	74.6	76.6	80.0	82.3
red iron oxide		7.3	7.8	8.2	8.6	9.0	9.4
mica (Micromica)		51	55.2	57.8	59.5	62.1	63.7
sodium carboxymethyl cellulose		1.0	1.0	1.0	1.0	1.0	1.0
barium metaborate		47.8	51.9	54.1	55.8	58.2	59.6
water		42.5	83.2	104.2	155.0	138.9	153
pigment volume concentration (%)		60	65	68	70	73	75

Three series of coated glass panels were formed as in the preceding examples, and after curing at ambient temperatures for six days, one series of panels were evaluated for abrasion resistance in accordance with the procedure of Example 1.

Example No.	No. of Double Finger Rubs	Water Spot*
22	>200	Severe whitening resembling bloom
23	>200	Severe whitening resembling bloom
24	>200	Moderate whitening
25	>200	Slight whitening
26	85	Severe whitening
27	100	Severe whitening

* One drop of tap water is placed upon the coating and allowed to dry.

The light reflectance of the unsoaked series of panels, aged 6 days was compared with a series of panels soaked as in the abrasion test.

	Light Reflectance		
Example No.	Unsoaked	Soaked	Color Change Value**
22	31.44	Whitening	—
23	27.68	Whitening	—
24	26.97	30.06	125%
25	27.58	30.69	126%
26	33.42	35.74	117%
27	34.10	36.51	117%

** An unsoaked area being compared to a soaked area using the Kubelka-Monk

$$\frac{K}{S}$$

value raised to the 1.125 power · $\frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty}$,

where R_∞ is the reflectance of an infinitely thick layer.

Examples 28—30.

Coating compositions were prepared by formulating the following ingredients:

		Parts by Weight		
Ingredients	Ex. No.	28	29	30
potassium silicate solution (as Ex. 11—14)		350	350	350
sodium aluminate solution[1]		51.1	51.1	51.1
organic phosphate wetting agent (strodex PK—90)		0.6	0.6	0.6
silicone antifoam agent (SWS 214)		1.5	1.5	1.5
TiO_2 (CLNC grade)		105	—	—
Silica (Minusil 15)		—	—	68
Alumina (Alcoa H—710)		—	82	—
Mica (Micromica)		90	90	90
Magnesium aluminum silicate (Attagel 40)		10	10	10

[1] 200 parts water, 2.3 parts sodium aluminate, 2.0 parts KOH, stirred until clear.

Two series of coated glass panels were formed as in the preceding examples, and after curing at ambient temperatures for five days, both series were evaluated for abrasion resistance in accordance with procedure of Example 1.

Example No.	No. of Double Finger Rubs	Comment
28	4	Chipped from edges — anomolous adhesive loss
28	>200	
29	156	
29	>200	
30	>200	
30	>200	

After three days at 160°F no hard gel was noted in 1/2 pint packages.

Example 31.

A curable coating composition was prepared using conventional paint mixing techniques and equipment by admixing 231.3 grams of an aqueous potassium silicate solution having an SiO_2:K_2O ratio of 3.3:1 and a solids content of 38.8 percent by weight available commercially under the designation Kasil No. 6 from Philadelphia Quartz Company, 5.03 grams of sodium tetraborate, 180 grams of water, 105.0 grams of titanium dioxide, 72.5 grams of mica and 10.0 grams of Attagel 40 (a magnesium aluminum silicate thixotropic agent available from Engehard Minerals Company).

The resulting composition was drawn down on duplicate sets of glass panels using a 3 mil Bird Bar. One set of coated glass panels was cured by air drying at ambient temperature for two days while the second set of coated panels was cured by air-drying at ambient temperature for six days.

The cured coatings were then evaluated for wet abrasion resistance by soaking the coating panels in water (temperature 70°F ± 5°F) for one hour and then rubbing the surface of the cured coating with a water soaked cloth. The web abrasion resistance was evaluated by determining the number of back and forth finger rubs (recorded as double finger rubs) needed to abrade the coating surface and expose the substrate.

The coating cured by air-drying at ambient temperature for 2 days abraded after 2 double finger rubs while the same coating cured by air-drying at ambient temperature for 6 days did not abrade after 200 double finger rubs.

Examples 32—39.

Coating compositions were prepared by formulating the following ingredients using ordinary coating formulation and pigment grinding techniques:

Ingredients Ex. No.	32	33	34	35	36	37	38	39
	Parts by Weight							
Aqueous potassium silicate solution[1]	350	350	350	350	350	350	350	350
water	73	73	73	73	73	73	73	73
sodium borate	5.0	2.5	3.75	1.25	6.75	0.62	2.5	2.5
organic phosphate wetting agent[2]	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
silicone antifoam agent (SWS 214)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TiO_2 (CLNC grade)	105	105	105	105	105	105	–	–
alumina (Alcoa H–710)	–	–	–	–	–	–	82	–
silica (Minusil 15)	–	–	–	–	–	–	–	68
mica (Micromica)	90	90	90	90	90	90	90	90
magnesium aluminum silicate (Attagel 40)	10	10	10	10	10	10	10	10

[1] A solution having an $SiO_2:K_2O$ ratio of 3.93:1 and a solids content of 29.1 percent by weight, available from Philadelphia Quartz Company.

[2] PK–90 – an organic phosphate available from Dexter Chemical Company.

A series of coated glass panels were prepared by drawing down each of the above coatings on glass panels using a 3 mil Bird Bar. After curing at ambient temperature for five days, the cured coatings were evaluated for wet abrasion resistance as in Example 31.

Example No.	No. of Double Finger Rubs
32	>200
33	>200
34	>200
35	>200
36	>200
37	>200
38	>200
39	>200

After 3 days at 160°F no hard gel was noted in 1/2 pint packages.

Example 40.

A curable coating composition was prepared using conventional paint mixing techniques and equipment by admixing 231.0 grams of an aqueous potassium silicate solution having an SiO_2:K_2O ratio of 3.3:1 and a solids content of 38.8 percent by weight (available commercially under the designation Kasil No. 6 from Philadelphia Quartz Company), 1.8 grams of zinc chloride, 2.8 grams of potassium hydroxide, 180 grams of water, 105.0 grams of titanium dioxide, 72.5 grams of mica and 10.0 grams of Attagel 40. (The zinc chloride and potassium hydroxide form the latent insolubilizer, potassium zincate).

The curable composition resulting from the above procedure was drawn down on several sets of glass panels using a 3 mil Bird Bar. One set of coated glass panels was cured by air drying at ambient temperature for one day, a second set of coated glass panels was cured by air drying at ambient temperature for 6 days.

The cured coatings were then evaluated for wet abrasion resistance by soaking the coated glass panels in water (temperature 70°F. ± 5°F.) for one hour and then rubbing the surface of the cured coating with a water soaked cloth. The web abrasion resistance was evaluated by determining the number of back and forth finger rubs (recorded as double finger rubs) needed to abrade the coating surface.

The coating cured by air drying at ambient temperature for two days abraded after 3 double finger rubs while the coating cured by air drying at ambient temperature for 6 days did not abrade after 200 double finger rubs.

Examples 41—48.

Coating compositions were prepared by formulating the following ingredients using ordinary coating formulation and grinding techniques:

	Parts by Weight							
Ingredients Ex. No.	41	42	43	44	45	46	47	48
Aqueous potassium silicate solution[1]	350	350	350	350	350	350	350	350
water	73	73	73	73	73	73	73	73
$ZnCl_2$	1.8	1.2	0.6	2.4	3.0	0.3	0.6	0.6
KOH	2.8	2.1	1.4	3.5	4.2	0.7	1.4	1.4
organic phosphate wetting agent[2]	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
silicone antifoam agent (SWS 214)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TiO_2 (CLNC grade)	105	105	105	105	105	105	—	—
alumina (Alcoa H–710)	—	—	—	—	—	—	82	—
silica (Minusil 15)	—	—	—	—	—	—	—	68
mica (Micormica)	90	90	90	90	90	90	90	90
magnesium aluminum silicate (Attagel 40)	10	10	10	10	10	10	10	10

[1] A solution having a SiO_2K_2O ratio of 3.93 : 1 and a solids content of 29.1 percent by weight, available from Philadelphia Quartz Company.

[2] PK–90 – an organic phosphate available from Dexter Chemical Company.

A series of coated glass panels were prepared by drawing down each of the above coatings on glass panels using a 3 mil Bird Bar. After airing at ambient temperature for five days, the cured coatings were evaluated for wet abrasion resistance as in Example 45. (The zinc chloride and potassium hydroxide form the latent insolubilizer, potassium zincate).

Example No.	No. of Double Finger Rubs
41	>200
42	67
43	center of film 200 edges 40
44	>200
45	>200
46	>200
47	>200
48	>200

After 3 days at 160°F no hard gel was noted in 1/2 pint packages, Example Nos. 46, 49 and 50 had a heavy viscosity when stirred.

The following examples (A—L) illustrate the preparation of latent insolubilizing agents.

Example A.

Into a container equipped with a magnetic stirrer was charged 4.5 parts of sodium ethylenediaminetetraacetate (a compound designated as $Na_4EDTA{\cdot}2H_2O$, available in the form of a solid powder from the Fisher Company) and 150.0 parts of tap water. The charged ingredients were mixed until a clear solution was obtained. Then 3.3 parts of $Al_2(SO_4)_3{\cdot}18H_2O$ (available in the form of a solid powder from the Fisher Company) were added to the container and mixing continued for about 2.5 hours. The resultant Al^{+++}/EDTA solution after this extended mixing period was very turbid.

Example B.

Into a container equipped with a magnetic stirrer was charged 1.4 parts $SnCl_2$ and 18.5 parts of water. Then 3.1 parts of $Na_4EDTA{\cdot}2H_2O$ were added and the mixture stirred for 15 minutes. At this time, the solids did not dissolve. Following this, 18.5 parts of water and 4.2 parts of $Na_4EDTA{\cdot}2H_2O$ were added to the container with stirring. The resultant solution was nearly clear, exhibiting a light green color.

Example C.

This example illustrates the effect of using high levels of Sn^{++}/EDTA complex. Into a container equipped with a magnetic stirrer was charged 4.2 grams of $Na_4EDTA{\cdot}2H_2O$, 20 grams of water, 1.9 grams of $SnCl_2$ and 60 grams of an aqueous potassium silicate solution having an Sio_2:K_20 ratio of 3.1:1 and a solids content of 38.8 percent by weight, available commercially from the Philadelphia Quartz Company under the designation Kasil No. 6. The ingredients were stirred and a precipitate formed which did not completely dissolve. The produce was then evaluated in the composition of Example 4.

Examples D—F.

In these examples, a series of Al^{+++}/EDTA complex solutions were prepared utilizing varying amounts of Al^{+++} and EDTA.

The solutions were prepared by mixing the following ingredients in a container equipped with magnetic stirrer:

Ingredients	Ex. No.	D	E	F
		Parts by Weight		
$Al_2(SO_4)_3 \cdot 18H_2O$		3.90	5.90	7.80
$Na_4EDTA \cdot 2H_2O$ (as in Example A)		5.46	8.20	10.92
H_2O		30.00	30.00	30.00

After mixing, the solution of Example D was nearly clear while those of Examples E and F were cloudy. The above solutions were formulated into coating compositions, cured and the coatings then evaluated for wet abrasion and water resistance as shown in Examples 5—7.

Examples G—I.

In these examples, a series of Sn^{+++}/EDTA complex solutions were prepared utilizing various levels of SN^{++} and EDTA.

The solutions were prepared by mixing the following ingredients in a container equipped with a magnetic stirrer:

Ingredients	Ex. No.	G	H	I
		Parts by weight		
$SnCl_2$		2.50	3.75	5.00
$NaEDTA \cdot 2H_2O$ (as in Example A)		5.46	8.20	10.92
H_2O		40.00	40.00	40.00
HCl (12 *N* aqueous solution)		2.00	2.00	2.00

After mixing, the solutions of Examples G and H were nearly clear while that of Example I was cloudy.

The above solutions were formulated into coating compositions, cured and the coatings then evaluated for wet abrasion and water resistance as shown in Examples 8—10.

Examples J—L.

These examples illustrate the preparation of Fe^{+++}/EDTA, Cr^{+++}/EDTA and Al^{+++}/EDTA complexes.

The complex solutions were preared by mixing the following ingredients in a container equipped with a magnetic stirrer:

Ingredients	Ex. No.	J	K	L
		Parts by Weight		
$Al_2(SO_4)_3 \cdot 18H_2O$		3.30	—	—
$FeCl_3$		—	2.70	—
$CrCl_3$		—	—	2.70
$Na_4EDTA \cdot 2H_2O$ (as in Example A)		6.00	6.00	6.00
H_2O		164.00	164.00	164.00

After mixing, the solution of Example J was clear and colorless, the solution of Example K was clear and brown in color and the solution of Example L was cloudy and purple in color.

The above solutions were formulated into coating compositions, cured and the coatings then evaluated for wet abrasion and water-resistance.

The following examples (49—61) illustrate curable pigmented compositions prepared from the complexes of the foregoing examples (i.e., A—L) and water-soluble silicates.

Example 49.

Into a container equipped with a 2" Cowles (registered Trade Mark) blade mixer was charged 231.5 parts of an aqueous potassium silicate solution having an $SiO_2:K_2$ ratio of 3.3:1 and a solids content of 38.8 percent by weight, available commercially from the Philadelphia Quartz Company under the designation Kasil No. 6. Then, 157.8 parts of the complex solution of Example A were added to the container with mixing. Following this addition, 10.4 parts of water and 18.3 parts of a surfactant mixture consisting of 7.5 parts of water, 1.2 parts of Foamaster VL (a defoamer available from Nopco Chemical Company), 4.0 parts of Antarox BL 240 (a non-ionic surfactant available from GAF Corporation) 3.6 parts of PK—90 solution (a solution consisting of 0.6 part of PK—90, an organic phosphate available from Dexter Chemical Corporation, and 3.0 parts water) and 2.0 parts of a 50 percent aqueous solution of potassium tripolyphosphate (Stauffer Chemical Company) were added. Then, 72.5 parts of mica, 94.7 parts of titanium dioxide, 12.2 parts of red iron oxide, and 10.0 parts of Attagel 40 (magnesium aluminum silicate thixotropic agent available from Engelhard Minerals) were individually added to the container with stirring. Finally, 10.0 parts of water and 1.0 part of Foamaster VL were added to the container.

The curable composition resulting from the above process was drawn down on duplicate sets of glass panels using a 3-mil Bird Bar. One set of coated glass panels was cured by air drying for 1—2/3 days at room temperature and heating in a 120°F. oven for 11—1/3 days. A second set of coated glass panels was cured by air drying at ambient temperature for 13 days.

The cured coatings were then evaluated for wet abrasion resistance by soaking the coated glass panels in water for one hour and then rubbing the surface of the film with a water soaked cloth. The web abrasion resistance was evaluated, determining the number of double finger rubs. In this test, both sets of coated panels passed over 200 double finger rubs without abrading the surface, thereby indicating that the composition forms films having excellent wet abrasion and water resistance. A similar composition containing no metal complex failed this test at one and 16 double finger rubs in two trials.

Example 50.

Into a container equipped with a 2" Cowles blade mixer was charged 231.5 parts of an aqueous potassium silicate solution having an $SiO_2:K_2O$ ratio of 3.3:1 and a solids content of 38.8 percent by weight available commercially from the Philadelphia Quartz Company under the designation Kasil No. 6. Then, 157.8 parts of the complex solution of Example A were added to the container with mixing. Following this addition, 10.4 parts of water and 18.3 parts of a surfactant mixture consisting of 7.5 parts of water, 1.2 parts of Foamaster VL (a defoamer available from Nopco Chemical Company), 4.0 parts of Antarox BL 240 (a non-ionic surfactant available from GAF Corporation), 3.6 parts of PK—90 solution (a solution consisting of 0.6 part of PK—90, an organic phosphate available from Dexter Chemical Corporation and 3.0 parts of water), and 2.0 parts of a 50 percent aqueous solution of potassium tripolyphosphate were added. Then, 72.5 parts of mica, 12.5 parts of sodium carboxymethyl cellulose, 94.7 parts of titanium dioxide, 12.2 parts of red iron oxide, and 10.0 parts of Attagel 40 (a magnesium aluminum silicate thixotroping agent available from Engelhard Minerals) were individually added to the container with stirring. Finally, 10.0 parts of water and 1.0 part of Foamaster VL were added to the container.

The curable composition resulting from the above process was drawn down in films on duplicate sets of glass panels, cured, soaked and evaluated for wet abrasion and water resistance in essentially the same manner as in Example 49. In this test, the set control panels cured by air drying for 1—1/3 days and heating in the oven for 11—1/3 days at 120°F. passed 130 double finger rubs while the set of coated panels cured by air drying for 13 days at ambient temperature passed 150 double finger rubs, again indicating excellent wet abrasion and water resistance.

Example 51.

Into a container equipped as in Examples 1 and 2 was charged 114.0 parts of the potassium silicate solution of Example 49 (i.e., Kasil No. 6). Then, the complex solution of Example B (45.7 parts) was added with with stirring. At this point a precipitate formed, which upon additional stirring dissolved. Then 90.7 parts of a pigment paste prepared in conventional manner and consisting of 48.7 percent of H_2O, 0.5 percent of aminomethyl propanol, 0.5 percent of Foamaster G (a defoamer available from Nopco Chemical Company), 37.2 percent of TiO_2, 10.4 percent of mixa and 2.7 percent of Attagel 40 was added. The resultant composition was drawn down in a 3 ml thickness as in previous examples and cured by drying in air at ambient temperature for 24 hours. Wet abrasion and water resistance of the cured films was evaluated by immersing one half (1/2) of the coated panel in water for one hour and then rubbing both the soaked an unsoaked areas of the coated panel with a wet cloth. In this test, both the soaked and unsoaked areas of the coated panel passed 200 double finger rubs without abrasion of the film, indicating that the composition forms cured films having excellent wet abrasion and water resistance.

Example 52.

This example illustrates the effect on coating composition properties of using the Sn^{++}/EDTA complex of Example C.

Into a container equipped as in Example 49 were charged 114.0 parts of the aqueous potassium silicate solution designated Kasil No. 6 and 86.1 parts of the complex solution of Example C. Upon mixing these ingredients, a gel formed. The addition of 24.0 parts of water to the gel caused it to thin out but the resultant composition remained cloudy even after stirring for an additional hour. Then, 71.8 parts of a pigment paste, prepared in conventional manner, containing 34.3 percent of water, 0.7 percent of aminomethyl propanol, 0.7 percent of Foammaster G, 47.5 percent titanium dioxide, 13.4 percent of mica and 3.4 percent of Attagel 40 was added to the containers with stirring.

The resultant composition was drawn down on a glass panel using a 3-ml Bird Bar and cured by air drying at ambient temperature for 24 hours. The coated glass panel was then partially immersed in water and allowed to soak for one hour. Both the soaked area and the unsoaked areas of the coated panel were then evaluated for wet abrasion and water resistance by rubbing the cured coating with a wet cloth. The unsoaked area of the film did not abrade after 200 double finger rubs while the soaked area abraded after 30 double finger rubs. This example shows that the use of excess quantities of insolubilizing agent in the composition not only affects the package stability of the uncured composition but also adversely affects the wet abrasion and water resistance of the cured composition.

Examples 53—55.

These examples illustrate curable coating compositions formulated from potassium silicate and the complex solutions of Examples D—F. In these examples, the compositions were prepared by mixing the following ingredients in a container equipped with a 2″ Cowles blade mixer:

Ingredients	Ex. No.	Parts by Weight 53	54	55
Aqueous potassium silicate of Example 49 (Kasil No. 6)		231.30	231.30	231.30
Complex solution of Example D[(1)]		29.36	—	—
Complex solution of Example E[(2)]		—	44.10	—
Complex solution of Example F[(3)]		—	—	48.70
Aminomethyl propanol		1.00	1.00	1.00
Foamaster G		2.00	2.00	2.00
TiO_2		112.00	112.00	112.00
Mica		35.00	35.00	35.00
Attagel 40		22.50	22.50	22.50
Sodium carboxymethyl cellulose		7.50	7.50	7.50
H_2O		158.50	158.50	158.50

(1) Upon addition, the composition became very slightly cloudy.

(2) Upon addition, the composition became cloudy and stiff.

(3) Upon addition, the composition became cloudy and stiff.

The curable coating compositions resulting from mixing the above ingredients were drawn down on duplicate glass panels using a 3-ml Bird Bar, cured by drying in air at ambient temperature for various time periods and then evaluated for wet abrasion and water resistance using the procedure of Example 49. Test conditions and test results are shown in Table I.

TABLE I

Example No.	Cure Conditions'	Water Soak	Cure Time (# Double Finger Rubs) 1 Day	3 Days	4 Days	7 Days
53	Ambient temperature — air dry	1 hr.	20	71	90	116
54	Ambient temperature — air dry	1 hr.	5	10	10	3
55	Ambient temperature — air dry	1 hr.	2	6	3	5

The above examples again illustrate that high levels of insolubilizing agent in the compositions cause instability in the uncured composition and adversely affect the wet abrasion and water resistance of the cured compositions.

Examples 56—58.

These examples illustrate curable coating compositions formulated from potassium silicate and the complex solutions of Examples G—I.

In these examples, the compositions were prepared by mixing the following ingredients in a container equipped with a 2″ Cowles blade mixer:

Ingredients	Ex. No	Parts by Weight 56	57	58
Aqueous potassium silicate of solution Example 49 (Kasil No. 6)		231.30	231.30	230.30
Complex solution of Example G⁽¹⁾		49.96	—	—
Complex solution of Example H⁽²⁾		—	53.95	—
Complex solution of Example I⁽³⁾		—	—	57.92
Aminomethyl propanol		1.00	1.00	1.00
Foamaster G		2.00	2.00	2.00
TiO_2		112.00	112.00	112.00
Mica		35.00	35.00	35.00
Attagel 40		22.50	22.50	22.50
Sodium carboxymethyl cellulose		7.50	7.50	7.50
H_2O		158.50	158.50	158.50

(1) Upon adding to potassium silicate, composition remained clear.

(2) Upon adding to potassium silicate, composition remained nearly clear but some lumps formed which broke up when thinned with H_2O

(3) Same observation as in (2) above.

The curable compositions resulting from mixing the above ingredients were drawn down on duplicate glass panels using a 3-ml Bird Bar, cured by drying in air at ambient temperature for various time periods and then the cured coatings were evaluated for wet abrasion and water resistance. Test conditions and results are shown in Table II.

TABLE II

Example No.	Cure Conditions	Water Soak	Cure Time (# Double Finger Rub) 1 Day	3 Days	4 Days
56	Ambient temperature — air dry	1 hr.	11	200 +	200 +
57	Ambient temperature — air dry	1 hr.	5	7	7
58	Ambient temperature — air dry	1 hr.	4	7	7

The above examples further illustrate the adverse effect of high levels of insolubilizing agent on the wet abrasion and water resistance of the cured composition.

Examples 59—61.

These examples illustrate curable coating compositions formulated from potassium silicate and the Al^{+++}/EDTA, Fe^{+++}/EDTA and Cr^{+++}/EDTA complexes of Examples J—L.

In these examples, the compositions were prepared by mixing the following ingredients in a container equipped with a 2″ Cowles blade mixer:

Ingredients	Ex. No	Parts by Weight 59	60	61
Aqueous potassium silicate solution of Example 49		231.0	231.0	231.0
Complex solution of Example J		173.3	—	—
Complex Solution of Example K		—	172.7	—
Complex solution of Example L		—	—	172.7
Surfactant mixture of Example 49		14.1	14.1	14.1
Foamaster VL		2.2	2.2	2.2
Mica		72.5	72.5	72.5
Sodium carboxymethyl cellulose		12.5	12.5	12.5
TiO_2		94.7	94.7	94.7
Red Iron Oxide (Fe_2O_3)		12.2	12.2	12.2
Attagel 40		10.0	10.0	10.0

The curable compositions resulting from mixing the above ingredients were drawn down on glass panels using a 3-mil Bird Bar, cured by drying in air at ambient temperature for ten (10) days and then the cured coatings were evaluated for wet abrasion and water resistance as in Example 54. The cured composition of Example 59 passed up to 60 double finger rubs, the cured composition of Example 60 passed up to 14 double finger rubs and the cured composition of Example 61 passed over 200 double finger rubs.

The following examples (i.e., 62—63) illustrate unpigmented (i.e., clear) compositions.

Examples 62—63.

In these examples, an unpigmented control composition (Example 67) composed of only an aqueous potassium silicate solution was compared to a curable unpigmented composition (Example 68) composed of an aqueous potassium silicate solution and an Al^{+++}/EDTA complex.

The compositions were prepared by mixing the following ingredients:

Ingredients	Ex. No.	Parts by Weight 62 (Control)	63
Kasil no. 1*		308.0	308.0
H_2O		40.0	40.0
$Al_2(SO_4)_3 \cdot 18H_2O$		—	3.3
$Na_4EDTA \cdot 2H_2O$ (as in Example A)		—	6.0

*An aqueous potassium silicate solution having an SiO_2:K_2O ratio of 3.93:1 and a solids content of 29.1 percent by weight, available commercially from the Philadelphia Quartz Company.

The compositions resulting from mixing the above ingredients were drawn down on glass panels using a 3-mil Bird Bar and cured by drying in air at ambient temperature for 24 hours. The coated panels containing the cured coatings were then soaked in water for ten (10) minutes and evaluated for wet abrasion and water resistance as in Example 49.

The coating formed from the control composition (i.e., Example 67—no complex) failed (i.e., was removed) after only two double finger rubs while the cured coating formed from the test composition (i.e., Examples 63—Al^{+++}/EDTA complex) passed over 100 rubs without failure.

Compositions of similar stability are formed with Al^{+++}, Fe^{+++}, Cr^{+++} and Sn^{++} with ligands of the type: diethylenetriaminepentaacetate, N-(hydroxyethyl)-ethylenediaminetriacetate, nitrilotriacetate, 1,3-propanediaminetetraacetate.

WHAT WE CLAIM IS:—

1. A curable composition comprising an aqueous solution of a water-soluble silicate and a water-soluble latent insolubilizing agent formed from a metal ion selected from Al^{+++}, Fe^{+++}, CR^{+++} and SN^{++}, and a ligand selected from ethylenediaminetetraacetate, diethylenetriaminepentaacetate, (N-(hydroxyethyl)-ethylenediaminetriacetate, nitrilotriacetate and 1,3- propanediaminetetraacetate; or an alkali metal or quaternary ammonium borate, aluminate or zincate; wherein the amount of said insolubilizing agent included in said composition is from 0.1 percent to 5.0 percent based on the combined weight of water soluble silicate and water-soluble latent insolubilizer.

2. A curable composition as claimed in claim 1 in which the amount of insolubilizing agent is from 0.25 to 2.0 percent based on said combined weight.

3. A curable composition as claimed in claim 1 or 2 further containing a water-soluble thickener.

4. A curable composition as claimed in claim 3 wherein said water-soluble thickener is a thickener which has been rendered water-soluble by reaction of carboxyl groups contained in said thickener with a base.

5. A curable composition as claimed in any one of claims 1 to 4 further containing a pigment or pigments.

6. A curable composition as claimed in claim 5 wherein said pigments include titanium dioxide or mica or a mixture thereof.

7. A curable composition as claimed in any one of claims 1 to 6 further containing phosphate type surfactants.

8. A curable composition as claimed in any one of claims 1 to 7 wherein said water soluble silicates are selected from lithium silicate, potassium silicate, sodium silicate or quaternary ammonium silicates.

9. A curable composition as claimed in any one of claims 1 to 7 wherein said silicate is potassium silicate.

10. A curable composition as claimed in any one of claims 1 to 9 wherein the insolubilizing agent is stable at a pH of greater than 7.0.

11. A curable composition as claimed in any one of claims 1 to 9 wherein the insolubilizing agent is an alkali metal or quaternary ammonium aluminate.

12. A curable composition as claimed in any one of the preceding claims which contains an inorganic pigment selected from titanium dioxide, zirconium dioxide, alumina and tin oxide.

13. A curable composition as claimed in claim 1 and substantially as hereinbefore described with reference to any one of Examples 1 to 4, 6, 8 to 10 and 12 to 48.

14. A curable composition as claimed in claim 1 and substantially as hereinbefore described with reference to any one of Examples 49, 50, 51, 61 and 63.

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