



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/KP91/00010 (22) International Filing Date: 24 October 1991 (24.10.91) (30) Priority data: 90-2879 5 December 1990 (05.12.90) KP (71) Applicant (for all designated States except US): HUNGSONG CORPORATION [KP/KP]; Donghung Dong, Changgwang Street, Zungguyok, Pyongyang (KP). (72) Inventors; and (75) Inventors/Applicants (for US only) : HYONG, Kim, Gyu [KP/KP]; YUN, Chae, Jae [KP/KP]; 45, Ban, Ryusong Dong, Bodunamu Street, Zungguyok, Pyongyang (KP). (74) Agent: PYONGYANG PATENT & TRADEMARK AGENCY; P.O. Box 6, Pyongyang Central (KP).		(81) Designated States: AT (European patent), BE (European patent), CH, CH (European patent), DE, DE (European patent), DK, DK (European patent), ES (European patent), FR (European patent), GB, GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL, NL (European patent), NO, SE, SE (European patent), US. Published <i>With international search report.</i>
(54) Title: COMPLETELY INORGANIC, PERMANENTLY ANTI-CORROSIVE, INNOXIOUS ANTI-FOULING PAINT (57) Abstract This is a paint composed of denatured silicate as vehicle and aluminosilicate as dispersoid. Its chemical structure being made reticulated one due to silanol radical reaction, this paint forms a special, completely inorganic functional film close to organic high molecular one. This film prohibits the flow of ions of iron, thus performing anti-corrosive action and discomposing the secretion of sea adhesive organisms, amino acid calcium colloid to give innoxious anti-fouling effect. The paint is also applicable to inside and outside coating of structures and colors for pictures, which have permanent smokeless, humidity controlling, anti-bacterial, anti-static properties.		

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⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

Completely inorganic, permanently anti-corrosive,
innocuous anti-fouling paint

Present invention relates to a completely inorganic,
permanently anti-corrosive, innocuous anti-fouling paint.

Since it was opened up as a heat curing paint by name of DAYMETCOAT in 1937 (Australian patent No. 1042317), the water glass system paint has been developed through chemical curing method (US patent No. 246263, 1970) and self curing method (US patent No. 4086-616, phosphoric acid method, No. 2536-871, zinc oxide method). But, where it is used as an anti-corrosive paint, the corrosion was prevented by method of increasing the concentration of zinc without exception.

After the heat curing method appeared, water glass system paint has been considered to give an anti-corrosive effect for heavy duty, special purpose steel structure, especially in deserts and ocean environment. But, in most cases, it is used as a primer for coating or along with organic paint.

Phosphoric acid and phosphate, such as silicon polyphosphate, titanium phosphate and metal oxides such as calcium oxide, alumina, etc. are known as curing agent of water glass paint already reported, and glass fibre, carbon fibre etc. are proposed as its reinforcing agent. Besides, a lot of patents are suggested. But, main defect of water glass system paint (lack of waterproofness, of bendability, of gloss etc.) have not been solved yet. Therefore, organic-inorganic complex compounds are recommended or it is replaced with alkyl silicate paint.

In addition, no attempt has been made in any patent to solve anti-corrosive, anti-fouling problem by forming a special functional film of inorganic silicate.

Recently, international organizations for preventing pollution in the world have taken legal procedures to prohibit poisonous anti-fouling paint. However, still there is no effective innoxious paint appeared.

The object of this invention is to provide a completely inorganic, permanently anti-corrosive, innoxious anti-fouling paint based upon the study of corrosion mechanism of iron and the property of adhesively inhabiting organisms in the sea environment.

Another object of this invention is to provide a paint for coating inside and outside of structures and colors for pictures which have excellent adhesiveness, waterresistance, humidity control, anti-static, anti-bacterial property and permanently unfading colors.

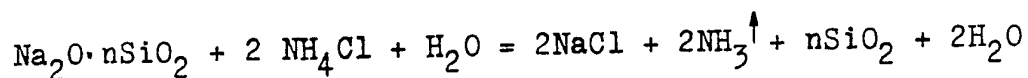
The latter object of the invention relates directly to a noble work for inheriting and developing more the valuable cultural heritages of our ancestors (everlasting, unfading colors) displayed in the mural of tombs and pictures of many colors and designs in the historic relics of Koguryo dynasty of our country.

According to the invention the paint is manufactured by various method in accordance with their uses.

First method

The solution of silicate $M_2O \cdot SiO_2$ of molar ratio (M_2O/SiO_2) 0,4-0,25 is mixed with ammon chloride so that molar ratio (NH_4Cl/SiO_2) can reach 0,2-0,5 (where $M = K, Na, Li, Rb$).

Then the following reaction occurs:



The silicagel obtained by above mentioned reaction is matured for a certain period of time and washed to get gel-state denatured ammonia silicagel ($x\text{H}_2\text{SiO}_3 \cdot \text{NH}_4\text{OH} \cdot y\text{H}_2\text{O}$) which absorbed ammonia gas. Its molar ratio ($\text{NH}_4\text{OH}/\text{SiO}_2$) is preferably 0,25-0,5. This mixture is mixed with silicate solution of molar ratio ($\text{M}_2\text{O}/\text{SiO}_2$) 0,25-0,5 at the ratio of 1-50:100 by weight. The resulting solution is dispersed with MX solution so that MX/SiO_2 can reach 0,01-0,05 to get denatured silicate solution of high viscosity (vehicle) (where, M: K, Na, Li, Rb, Ba, Zn, Ca; X: Cl, F, Br).

If above-mentioned denatured silicate solution is added with filler, dispersoid alumo silicate, metal oxides and metal powders, then a paint will be obtained. (where, the alumosilicate is $\text{M(I)}_2\text{O} \cdot \text{M(II)}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot m\text{H}_2\text{O}$ (M(I) and M(II) are monovalent and bivalent metallic cations, n is molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$, m is number of mol of water). Molar ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$)

is preferably in the range of 0,5-20, molar ratio ($\text{Na}_2\text{O}/\text{CaO}$) is preferably in the range of 1-10, the amount of ion exchange being 5-40 mg equivalent/100 g. The grain size of the filler is preferably 250-300 mesh. The vehicle is added preferably with alumo-silicate, one or two kinds of metal oxides of among ZnO , TiO_2 , Fe_2O_3 , BaO , Al_2O_3 , one or two kinds of metallic powders of among Zn, Fe, Al and Cu at the proportion of 30-40, 0-20, 0-20 weight % respectively.

If this paint is applied, a film having a capacity of exchanging and absorbing ions is obtained.

According to the molar ratio of filler and amount of its addition, the ion absorbing capacity of film changes in the range of 90-110 mg equivalent/100 g, iron exchanging capacity being 10-30 mg equivalent/100 g.

If a paint is made in this way and applied to the bottom of a ship, inorganic film is obtained, which is proved to have an absorbing capacity 3 times higher than natural zeolite in terms of absorption amount of cation, in particular Ca^{2+} (see table 1).

It was proved by infrared absorption spectrum analysis, X-ray diffraction analysis, X-ray photoelectron analysis, differential thermal analysis that the film has a three dimensional reticular structure capable of performing the function of ion exchange and absorption.

Adhering to the bottom of a ship, the organism secretes an adhesive substance, amino acid calcium colloid, which becomes a strong high molecular adhesive on the surface of the object and firmly adheres thereto.

As the surface of the film comprises very active alkali metal cations, it is able to easily exchange with other metallic cations. Therefore, the film absorbs Ca^{2+} away from amino acid calcium colloid solution of adhesive secretion product of sea adhesive organisms, thus weakening the adhesive strength of the adhesive organisms and making them unable to inhabitate.

Table 1
Comparison of ion absorbability of zeolite and inorganic film

Capacity of absorption (mg equivalent/100 g)								Exchanging component	Exchanging-absorbing component
of natural zeolite						of film			
No. 1	No. 2	specimen No. 3	No. 4	No. 5	No. 6	No.1	No.2		
40,35	41,45	40,50	60,55	61,35	59,35	47	48	Na ⁺	NH ₄ ⁺ → Na ⁺
21,74	21,74	20,74	25,74	27,94	17	17,	17	Na ⁺	Na ⁺ → NH ₄ ⁺
40,83	40,84	41,74	41,41	40,83	40,56	119,38	109,38	Ca ²⁺	NH ₄ ⁺ → Ca ²⁺

Table 2
Capacity of Ca ion absorption and exchange of film

Absorption capacity per 100 g	Absorption capacity per 1 cm ²	Exchange capacity per 100 g	Exchange capacity per 1 cm ²	Equivalent of secreting liquid of sea adhesive organism
100 mg equiv.	0,06 mg equiv.	17 mg equiv.	0,01 mg equiv.	2×10^{-5} mg equiv, per 1 cm ²

As is seen in the table 2, the capacity of exchange per 1 cm² of film is 0,01 mg equivalent and amount of calcium secreted by sea adhesive organism is 2×10^{-5} mg equivalent, these figures show that calcium exchangeability of film is far higher.

Therefore, not only the film has the capacity to absorb any amount of calcium secreted by sea adhesive organisms, including epiphytes, but also desorption-absorption process of calcium and sodium continues due to the constant reverse reaction in the sea water. Therefore, as long as film exists, the anti-fouling capacity against sea adhesive organisms, including epiphytes is permanent.

The function of film to protect iron from corrosion is also explained by the mechanism of absorbing and fixing the ions by prohibiting the flow of iron ions due to the capacity of absorption of ion.

The X-ray photoelectron analysis of film is shown in the annexed picture. It shows that the additives bond chemically to form a passivating film.

Embodiment

The vehicle is obtained according to the first method. This vehicle is mixed with filler of following composition and the resulting paint is applied to specimens and bottom of a ship and cured for a week, followed by exposure test and actual test.

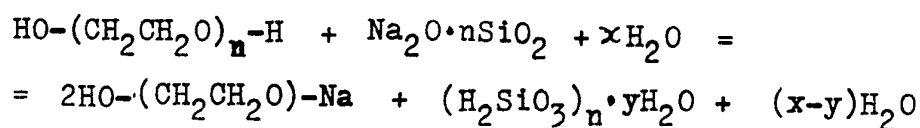
Composition: (by weight %)

Vehicle	40-60
Alumosilicate	20-30
Metal oxide	5-20
Zinc powder	5-16

The result shows that anti-fouling and anti-corrosive function of film has still been maintained for 15 years until now since the beginning of the actual test.

Second method

Polyethylene glycol ($n=1-2000$) is added to silicate solution having molar ratio $(M_2O/SiO_2)=0,4-0,25$. The former causes a neutralization and polysilicate elastomer (PSE) is obtained.



Precipitated PSE is dispersed into silicate solution so that molar ratio (PSE/SiO_2) can be 0,1-10,0 and then aluminium salt solution is added thereto so that molar ratio (Al_2O_3/SiO_2) can be 0,01-5,0 and heated at 100 °C to get vehicle.

This vehicle is mixed with barium sulphate, calcium phosphate, 1-2 kinds of metal oxides such as alumina, titanium white, zinc oxide etc. at the proportion of 5:1-10 by weight, which is made paste state, thus obtaining excellent smokeless, humidity controlling, anti-bacterial, anti-static paint needed for painting inside and outside of structures or colors for pictures.

The paint thus made is applicable to fabrics, concrete plate, glass, iron, slate and stone etc., excluding resin and oil colors' under-coating plate.

Embodiment

The vehicle obtained according to the second method is mixed with dispersoid of following composition and applied to cement plate and cured for one week:

Vehicle	40-60 % (by weight)
Titanium oxide	5-10 % " "
Zinc oxide	5-10 % " "
Barium sulphate	10-25 % " "

Table 3

Main properties of film			
Humidity control property	Anti-bacterial property	Anti-static property	Fire-resistance
5-7 g/m ² ·h·atm	Passed test of JIS 279 Passed exposure test for 8 years	10 ⁸ ohm	No change at 1000 °C

As is seen in table 3, the paint for decoration of inside and outside of building and structure has excellent humidity control, anti-bacterial, anti-static properties and is water-proof and smokeless. Therefore, its service time is very long, and it provides a good hygienic environment. Further, it is of completely inorganic, so it has an anti-aging property, too.

Actual test

When organic paint was applied as a painting material for inside and outside decoration of building, it grew moldy in a month in the mold-growing environment(at humidity of 90 % or so, temperature of 20-30 °C) and was contaminated within a year, which caused repainting unavoidably.

Though the paint has been used for inside-outside coatings and also for colors of pictures according to the invention, still there has not been found any mold growing for 8 years since the actual test commenced and the surface of the object has not been contaminated yet even in the mold-growing environment.

Claims

1. Completely inorganic, permanently anti-corrosive, innoxious anti-fouling paint, characterized in that silicate solution of $M_2O \cdot n SiO_2$ (M: k, Na, Li, Rb) of molar ratio (M_2O/SiO_2) 0,4-0,25 is mixed with ammonium chloride so that molar ratio (NH_4Cl/SiO_2) can reach 0,2-0,5 to get silicagel, which is matured for a certain period of time and washed to get a gel-state mixture, which absorbed ammonia gas, i.e. ammonia silicate ($xH_2SiO_3 \cdot NH_4OH \cdot yH_2O$) of molar ratio (NH_4OH/SiO_2) 0,25-0,5, which is added to silicate solution $M_2O \cdot nSiO_2$ of molar ratio (M_2O/SiO_2) 0,25-0,5 at the ratio of 1-50:100, resulting denatured silicate colloidal solution is again dispersed with MX (M: Li, Na, K, Ba, Ca, Al; X: F, Br, Cl) so that molar ratio (MX/SiO_2) can reach 0,01-0,05 to get denatured silicate solution (vehicle), which being added with aluminosilicate, one or two kinds of metal oxides of among ZnO , TiO_2 , Fe_2O_3 , BaO , Al_2O_3 , and one or two kinds of metal powder to provide permanently corrosive, innoxious anti-fouling function.

2. Paint according to claim 1, characterized in that ammonia silicate of molar ratio (NH_4OH/SiO_2) 0,25-0,5 is added to silicate solution $M_2O \cdot nSiO_2$ of molar ratio (M_2O/SiO_2) 0,25-0,5 at the proportion of 1-50:100 by weight to get denatured silicate colloidal solution.

3. Paint according to claim 1 or 2, characterized in that the denatured silicate colloidal solution obtained by claim 2 is added with MX (so that molar ratio (MX/SiO_2) can reach 0,01-0,05 to get again denatured high viscosity silicate solution(vehicle).

4. Paint according to any of the claims 1 to 3, characterized in that its dispersoid, aluminosilicate $M(I)_2O \cdot M(II)O \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O$ (where M(I) or M(II) is monovalent or bivalent metallic cation n is molar ratio of SiO_2/Al_2O_3 , m is number of mol of water) has molar ratio (Na_2O/CaO) in the range of 1-10, molar ratio (SiO_2/Al_2O_3) in the range of 0,5-2,0, the amount of ion exchange in the range of 5-40 mg equivalent/100 g.

5. Paint according to any of the claims 1 to 4, characterized in that denatured sodium silicate solution is mixed with one or two kinds of metal oxides selected of among the group of ZnO , TiO_2 , Fe_2O_3 , BaO , Al_2O_3 , aluminosilicate powder and one or two kinds of metal powder selected of among Zn, Fe, Al, Cu by 0-20, 30-40, 0-20 weight % respectively.

6. Paint according to any of the claims 1 to 5, characterized in that its chemical structure forms three dimensional one on the surface of the object, thus decomposing amino acid calcium colloid, the adhesive secretion of adhesive organisms of ship and giving anti-fouling effect.

7. Paint according to any of the claims 1 to 6, characterized in that it gives innocuous anti-fouling effect without using poisonous material.

8. Paint according to any of the claims 1 to 7, characterized in that it gives anti-corrosive effect by prohibiting the flow of ions of iron.

9. Paint according to any of the claims 1 to 8, characterized in that it gives anti-corrosive, anti-fouling effect permanently until the service time of ship ends due to the reverse process of ion absorption and exchange in the sea water.

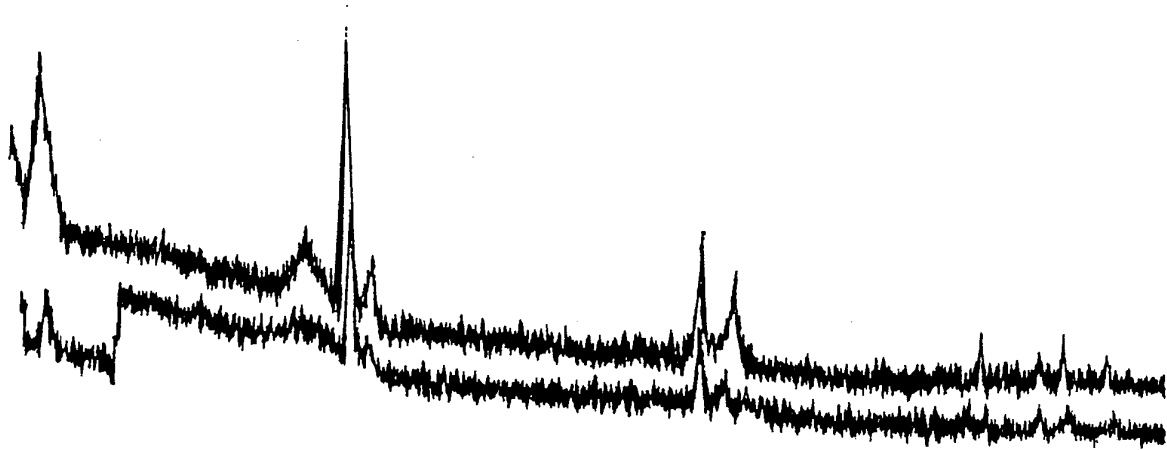
10. Completely inorganic paint for coating inside and outside of structure and colors for pictures, characterized in that polyethylene glycol is added to silicate solution of molar ratio (M_2O/SiO_2) 0,4-0,25 to get polysilicate elastomer (PSE), and that the latter is added to silicate solution so that molar ratio (PSE/SiO_2) can reach 0,1-10, the resulting solution being added with aluminium salt solution so that molar ratio (Al_2O_3/SiO_2) can reach 0,01-5,0 and heated at 100 °C to get denatured silicate vehicle colloidal solution, which being added with one or two kinds of pigments selected of among the group of barium sulphate, calcium phosphate, alumina, titanium white, zinc oxide and other pigments to get monoliquid paint of paste state adequate to making functional material for coating inside and outside of structures and colors for picture.

11. Paint according to claim 10, characterized in that polyethylene glycol ($n=1-2000$) is added to silicate solution of molar ratio (M_2O/SiO_2) 0,4-0,25 to get polysilicate elastomer (PSE).

12. Paint according to claims 10 or 11, characterized in that PSE is added to silicate solution in claim 11 so that molar ratio (PSE/SiO_2) can reach 0,1-10, and that the resulting solution is added with aluminium salt so that molar ratio (Al_2O_3/SiO_2) can reach 0,01-5,0 and heated at 100 °C to get denatured silicate vehicle colloidal solution.

13. Paint according to any of the claims 10 to 12, characterized in that the denatured silicate vehicle colloidal solution is added with one or two kinds of pigments selected of among the group of $BaSO_4$, $CaCO_3$, TiO_2 , and other pigments at the ratio of 5:1-10 by weight.

14. Paint according to any of claims 10-13, characterized in that it is applicable to fabrics, concrete plate, glass, steel plate, slate and stone with the exception of resin and primer plate for oil colors.



Picture. X-ray photoelectron analysis of film.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/KP 91/00010

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC 5		
C09D 1/02, 1/04, 5/08, 5/10, 5/14		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C09D 1/02, 1/04, 5/08, 5/10, 5/14	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 3893864 (EXXON RESEARCH AND ENGINEERING COMPANY), 8 July 1975 (08.07.75), column 2 lines 25-45, column 3 lines 25-55, column 4 lines 5-25, column 5 lines 5-20, column 7, example 9	1-9
A	GB, B, 1503153 (HOECHST AKTIENGESELLSCHAFT), 8 March 1978 (08.03.78), p.2 lines 15-60, 65-120, p.3 lines 10-30	1-9
A	JP, A, 54-133523, 17 October 1979 (17.10.79)	1-9
A	GB, B, 1459574 (DAI NIPPON TORYO KABUSHIKI KAISHA), 22 December 1976 (22.12.76), p.1 lines 50-75, p.3 lines 100-105, p.2 lines 5-85	1-2
A	JP, A, 58-108257, 28 June 1983 (28.06.83)	10-14
A	JP, B2, 57-14783, 26 March 1982 (26.03.82)	10-14
A	Obzornaya informatsia "Silikatnye lakokraskochnye materialy", 1989, NIITEXIM (Moscow), p. 25	5
¹⁰ Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
18 February 1992 (18.02.92)	26 February 1992 (26.02.92)	
International Searching Authority	Signature of Authorized Officer	
ISA/SU	N. Snepelev	