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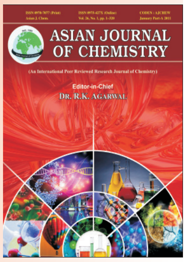

Synthesis of Emulsion of Water-Based Nano Silicon Oxide-Polyacrylic Ester†

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Emulsion of nanosized silicon oxide-polymerized acrylic ester with high solid content was prepared by soap-free emulsion polymerization, using silica sol as source of nanosized silicon oxide. The effects of the silica sol on the particle size, distribution of particle size, glass transition temperature, mechanical and applicable properties of emulsions were investigated. The results show that the particle size was reduced by joining the silicon sol, the latex particles were distributed evenly and the mechanical properties of the water-based coating had been also improved. The results of use test also show that the water-based coating is suitable for coatings of the walls and wood.

Keywords: Nanosized silicon oxide, Silica sol, Polyacrylic esters, Soap-free emulsion polymerization.

INTRODUCTION

Emulsions of polyacrylic esters are products of methacrylate, monomers of acrylate and vinyl, *etc*. by copolymerization methods[1]. Change of molar ratio of these monomers would affect the hardness and film-forming temperature of a film of the emulsion. The acrylate monomers could be produced into acrylic resin by polymerization reaction because of an existence of carbon-carbon double bond. The formation of saturated carbon-carbon single bond in main chain of molecules made that the resins had the good light, heat and chemical stability. Thus, the coating prepared by acrylate resin has super weathering and contamination resistance, *etc*. Furthermore, methacrylate has a methyl group on α position, belong to the typical asymmetric structure. It makes the copolymer molecular possess polarity. Thus, the physical and mechanical properties of the coating could be improved and the coating become hard, light fastness and weathering resistance further.

However, polyacrylic esters have still some defects, such as sticky in summer, crisp in winter and bad water resistance, *etc*.[2]. So far, the main methods of modification are such as soap-free emulsion polymerization[3,4], microemulsion polymerization[5], emulsion polymerization[6,7] and dispersion polymerization, *etc*.[8]. Some special performances could be obtained by participation of organosilicon[9-11], organofluorine[12], epoxy[13,14], polyurethane resin[15-17], *etc*. The emulsions of polyacrylic esters by modification and different polymerization processes has excellent cost performance and expansive prospect in leather paint, textile agent, coating material, adhesive, *etc*.

In recent years, hybrid polymers of nanosized oxide and emulsion of polyacrylic esters have received a significant amount of attention because of fabricability of emulsion of polyacrylic esters[18]. As a result, hybridization was made by modification of nanosized oxide to improve their defect in the use and make it more environmental friendly, practical, economic and functional.

In this article, surface-functionalized silica sol by triethylene glycol (TEG) was used as a stabilizer to participate in soap-free emulsion polymerization of acrylic esters and improve the compatibility between particles of silica sol and interface of polymer. The products of acrylic esters with high solid content were prepared by soap-free emulsion polymerization. The effects of processing conditions on the relevant properties of emulsions were discussed to determine stability mechanism of the soap-free emulsion, the best technological conditions and the best emulsion with good polymerization stability, mechanical stability, chemical stability and relevant performance.

EXPERIMENTAL

Modified silica sol was supplied by Jiangsu Rongchang Chemical Co., Ltd., China. Ammonium persulfate (APS), sodium bicarbonate ($NaHCO_3$), styrene (ST), butyl acrylate (BA), acrylic acid (AA) and methyl methacrylate (MMA) were purchased from Sinopharm Chemical Reagent Co., Ltd., China, respectively. Surfactant COPS-1 was purchased from Munzing chemical Co., Ltd., Germany. Thickening agent HEC250 and OS6040, dispersant SN5029 and BYK190, barium sulfate

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(1250 meshes) were purchased from Wuxi Handesen chemical Co., Ltd., China, respectively. pH regulator APM95, titanium dioxide 940, antifoaming agent TK340 were obtained from Guangzhou Hengyu Chemical Co., Ltd., China, respectively. Hydrated magnesium silicate (1200 meshes) was obtained from Changzhou Tianzhu Chemical Co., Ltd., China.

General procedure: According to the formulae shown in Tables 1 and 2, by changing the number of silica sol, the species of initiators and the number of functional monomers, soap-free nanosized silicon oxide-based composite emulsions with good stability and high solid content were prepared with using insufficient quantities of the monomers dripped to finish polymerization reaction and without emulsifying agent.

TABLE-1
EXPERIMENTAL FORMULA 1 WITH
DIFFERENT SILICON CONTENT (UNIT g)

Formula	1/0.0 (%)	2/2.5 (%)	3/5.0 (%)	4/7.5 (%)	5/10.0 (%)
Silica sol B	0	2.5	5	7.5	10
Deionized water	40	40	40	40	40
APS	0.32	0.32	0.32	0.32	0.32
$NaHCO_3$	0.4	0.4	0.4	0.4	0.4
Deionized water	80	80	80	80	80
ST	24	24	24	24	24
BA	24	24	24	24	24
AA	1.8	1.8	1.8	1.8	1.8
COPS-1	0.6	0.6	0.6	0.6	0.6

TABLE-2
EXPERIMENTAL FORMULA 2 WITH
DIFFERENT SILICON CONTENT (UNIT g)

Formula	1/0.0 (%)	2/2.0 (%)	3/3.0 (%)	4/4.0 (%)	5/5.0 (%)
Sol B	0	3.32	5	5	5
Deionized water	40	40	40	40	40
APS	0.42	0.42	0.32	0.42	0.42
$NaHCO_3$	0.53	0.53	0.4	0.53	0.53
Deionized water	41	80	80	80	41
MMA	32	16	24	32	32
AA	2.4	1.2	1.8	2.4	2.4
BA	31.92	16	24	31.92	31.92
COPS-1	0.8	0.4	0.6	0.798	0.8

A particular example is as follows. 5 g silica sol, B and 40 g deionized water was taken and put in a beaker with 100 mL graduations one after another and their mixture was stirred to disperse well (as dispersed system of silica sol). 0.32 g ammonium persulfate and 0.40 g sodium bicarbonate were added into another beaker with the same graduation one after another and their mixture was dissolved by using 80 g deionized water (as buffering solution of initiator). 24.00 g styrene, 24.00 g butyl acrylate monomers, 1.80 g acrylic acid and 0.60 g COPS-1 surfactant were also taken and put into the other beaker with the same graduation one after another and their mixture was also mixed evenly and sealed up (as monomers). The dispersed system of silica sol was introduced into a 500 mL, four-necked round bottom flask equipped with a thermometer, a mechanical stirrer and a condenser. With stirring speed of 120 rpm, buffering solution of initiator and 50 % of the monomers were put into the flask in turn and slowly, shaken and dispersed in 15 min. The flask was heated to 80 ºC with stirring over a period of 1 h and then the rest of the monomers were steadily added within 1.5 h. The reaction temperature was kept for 1 h. After materials cooled, drawn off and filtered, the product of a soap-free emulsion of modified silica sol and polyacrylic esters was obtained.

Detection method: Evaluation of emulsion film: Samples were taken down on a clean glass plate. The film was coated uniformly by using a spreader and dried to observe the smoothness and transparency.

Analysis of particle size of dynamic light scattering (DLS): Sample was diluted to one thousandth of concentration of origin with deionized water. After shaken and dispersed, 2 mL sample was removed into cuvette and measured. The laser wavelength of dynamic light scattering instrument is 658.0 nm and stable time is 1min and test temperature is 25 ºC and the number of scanning is 3 times.

Hardness of damped pendulum: The corresponding hardness value was obtained according to GB/T1730-2007.

Determination of adhesion: Adhesion test was finished according to GB/T1720-2007.

Determination of solid content: 2 g emulsion was coated uniformly on the tetrafluoroethylene-based pan. The pan was baked for 2 h at 105 ºC and then removed and weighed. It continued to bake and weigh the pan. It was until that the difference of quality is less than 0.01 g twice around. Calculation of solid content (S) is according to the ratio of mass of dry milk and mass of the emulsion.

Gel rate: After the polymerization being completed, the gel in sidewall of reactor and on a stirrer was collected and dried in an oven to a constant mass (G). The gel fraction (V) is the ratio of the G and mass of the total reaction materials.

Water absorption: The samples film were dried thoroughly and cut into the latex film with 20 mm × 10 mm × 1 mm and weighed (M1) and immersed into deionized water and weighed (M2) at set intervals often. Water absorption was calculated by difference of the mass around occupied with M1.

Analysis of FTIR spectroscopy: The emulsion was dried into film at 60 ºC. The films were analyzed by FTIR spectrometer with Perkin Elmer System 2000.

Thermal analysis of differential scanning calorimetry (DSC): Appropriate number of sample was placed in an aluminum crucible, using a 204F1 type differential scanning calorimeter (DSC) to test glass transition temperature of the samples. Range of temperature was from -30 ºC to 80 ºC.

Water-resistance of coating: Paints of the prepared polyacrylic esters were applied on the surface of iron, asbestos and wood substrate, respectively. At 60 ºC, they were baked in the oven until dry completely. The samples were put into the deionized water. The related phenomena were observed.

RESULTS AND DISCUSSION

Stabilization mechanism of nano silicon oxide/ polyacrylate latex: As is shown in Fig. 1, particles (diameter 20 nm) of surface-functionalized silica sol by triethylene glycol (TEG) was very easy to be adsorbed on the surface of monomer droplets and latex particle. Monomers of methyl methacrylate and butyl acrylate played a role of stabilizing agent in the reaction system. At 80 ºC, decomposition of the initiator ammonium persulfate initiated emulsion polymerization

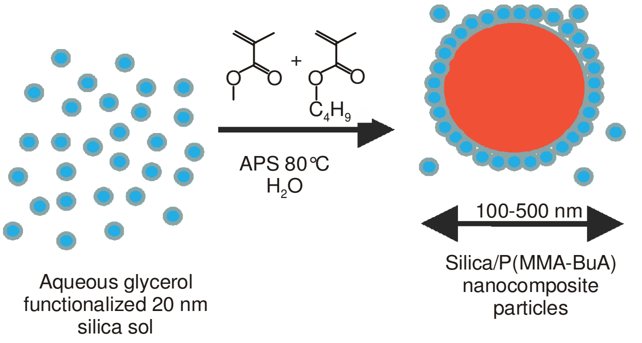

Fig. 1. Polymerization stability mechanism of nanosized silicon oxide/acrylate emulsion

reaction. Particles of surface-modified nanosized silicon oxide were coated around the polymer latex gradually. It played a space resistance effect and prevented agglomeration of the nanosized latex. So that the system was in steady state.

Properties of several modified silica sol and its influence on polymerization: In order to select the appropriate silica sol as the silicon source, pH values (determined by pH meter) and particle size (given before dilution, analyzed by DLS after dilution) and Zeta potential (also given by DLS) and the stability in the soap free emulsion polymerization of three alternative silica sol samples with different silicon content were determined, respectively.

Table-3 showed that before dilution particle size of the three kinds of silica sol A, B and C were 12, 20 and 30 nm, respectively. Though their stabilities were all good, they are difficult to maintain long-term stability, especially in polymerization process with high temperature, because of their stability effected by factors of ion concentration, pH value, temperature, dilution ratio, *etc*. The experimental had simulated process of soap free emulsion polymerization to measure particle size and zeta potential after dilution. The results show that after dilution diameters of nanosized SiO_2 particles were 40, 30 and 70 nm and zeta potential was -26, -31 and -25 mV, respectively. Furthermore, particle size of the silica was increased, the silica showing a conglobation and unstable trend of particles. In the three alternative silica sol, only change of particle size of silica sol B was small relatively and zeta potential had a minimum value, revealing existence of the thicker electric double layer, difficulty of agglomeration and good stability. The experiment also showed the best stability of emulsion polymerization. So the silica sol B was used as the silicon source.

Determination of polymerization conditions of nano- SiO_2/polyacrylate emulsion

TABLE-4
EFFECT OF REACTION TEMPERATURE
ON PERFORMANCE OF THE LATEX

Reaction temperature (ºC)	Appearance of latex	Conversion rate of monomer (%)	Slag rate (%)
70	Gray	70.2	0
75	White with blue	89.2	0
80	White with blue	99.1	0
85	White with blue	94.4	10

Effect of reaction temperature on performance of the latex: Table-4 showed that when the reaction temperature is 70 ºC, the latex was gray and the monomer showed the low conversion of 70.2 %. With increasing of the reaction temperature, conversion rate of the monomer was gradually increased. At reaction temperature of 80 ºC, the conversion rate reached the maximum value of 99.1 %. However, the reaction temperature was further increased to 85 ºC, gel began to appear and the Slag rate run up to 10 %, resulting in the decreasing of conversion rate of monomer.

The main reason is caused by thermally decomposition of the initiator ammonium persulfate. Conversions of the monomers were effected from decomposition temperature and half-life term of initiator. Low reaction temperature leaded to longer half-life term and residue of the initiator, resulting in slower reaction speed and lower conversion of monomers. However, the extreme high reaction temperature brought about the difficult to control the reaction. Monomers was easy to be started and induced to decompose by free radical, significantly resulting in aggregation and instability of the latex particles. The preferred reaction temperature of polymerization is 80 ºC.

Effect of reaction time on conversion of monomers: As can be seen from Table-5, after monomer being added dropwise, conversion of the monomer was increased with reaction time. At 1 h, conversion of the monomer reached up to 99.1 %. After that conversion of the monomers had no significant increase. So the preferred reaction time is 1 h.

TABLE-5
EFFECT OF REACTION TIME ON
CONVERSION OF MONOMERS

Reaction time (min)	0	15	30	45	60	75	90
Conversion of monomers (%)	86	90.2	94.6	98.4	99.1	99.1	99.2

Effect of functional monomers and initiator on stability of nanosized silica/acrylate emulsion: To examine the effect of the initiator on stability of solution, initiators V-50 and ammonium persulfate were used to initiate the polymerization reaction. It was found that under the same reaction conditions the V-50 would destroy the stability of the sol with low conversion rate, conversely the water-soluble ammonium persulfate was easier to initiate polymerization and play a stabilizing role. Because the fragment ions generated by decomposition of the water-soluble azo-based V-50 initiator was with a positive

TABLE-3
CHOICE OF MODIFIED SILICON SOL

Type of modified silica sol (secrecy)	Content of silicon oxide	pH	Particle size before dilution (nm)	Particle size after dilution (nm)	Zeta potential after dilution (mV)	Stability of polymerization
A	40 %	8	12	40	-26	Bad
B	35 %	3	20	30	-31	Good
C	30 %	8	30	70	-25	Bad

TABLE-6
EFFECT OF MONOMERS AND INITIATOR ON STABILITY OF NANOSIZED SILICA/ACRYLATE EMULSION

Serial number	Amount of silica sol (g)	Amount of APS (g)	Content of AA (%)	Content of SiO_2 (%)	Zeta potential (mV)	Gel (%)	Conversion of monomer	Storage stability
1	0	0.1	0	0	-15	7.3	×	×
2	0	0.2	0	0	-17	6.2	√	×
3	0	0.3	0	0	-20	5.5	√	×
4	5	0.2	1.8	10	-30	3.2	√	√
5	5	0.2	2.5	10	-34	0.3	√	√
6	5	0.2	3.7	10	-35	0.1	√	√
7	5	0.2	4.7	10	-36	0.2	√	√
8	2.5	0.2	3.7	5	-33	0.1	√	√
9	0	0.2	3.7	0	-33	5.0	√	×

charge, they would destroy stability of the sol by combining with the silica particle of which was a surface with a negative charge. However, after the ammonium persulfate decomposed, the fragment ions were negative charged. Therefore, the experimental data from 1-3 in Table-6, showed a good conversion of the monomers when the amount of ammonium persulfate was 0.2 g. At present, the initiator accounted 1 % of the number of monomers.d been significantly improved. However, an excessive carboxyl made the emulsion more hydrophilic.

The experiments from 4 to 7 in Table-6 had investigated the effect the number of monomers on stability of the reaction system with the different content of acrylic acid monomer and 10 % SiO_2. As can be seen from the table, with the increase of the number of acrylic acid, zeta potential of composite emulsion was also increased. At present, the electric double layer of surface of latex particle became thicker. Thus, stability of nanocomposite emulsion has made adversely affect on properties of the coating. The optimum number of acrylic acid was 3.7 %.

The experiments from 6 to 9 used acrylic acid of 3.7 % and initiator of 1 % to examine the effect the content of SiO_2 on properties of coating. The results show that the silica content of 10 and 5 % made a good polymerization and optimal storage stability, conversely for the silica content of 0 %, a large number of gel had emerged in polymerization process and the storage stability of them was also poor.

The stability mechanism of the nanosized silica/acrylate emulsion was as below. First, silica particles of functionalized surface were easily adsorbed on the latex particles, playing the role of steric stabilization. Secondly functional monomer namely acrylic acid provided carboxyl group for the latex particles by ionization to produce a negative charge. Thus mutual exclusion among the particles played a role in stabilizing the charge. In this experiment, two kinds of stabilization mechanisms were synergistic to stabilize the polymerization process and products.

Effect of content of silicon on particle size of the latex and distribution of particle size: Particle size and its distribution of latex are important properties of the emulsion of a polymer because they would influence performance and polymerization reaction rate of the polymer emulsion.

Effect of the content of SiO_2 on particle size and its distribution was showed in Fig. 2 and Table-7. As the content of SiO_2 is 0 %, average diameter of polymer latex particles was 487 nm with a polydispersity index (PDI) of 0.215. When silica sol was added into the polymerization system, particle size decreased and the distribution of particle size was significantly narrower. With a continuous increase of the amount of SiO_2, variation of particle size was not particularly obvious. However, they all show lower particle size value than the result of previous unmodified and less PDI value. Addition of SiO_2 decreased the particle size of the latex and made them more uniform.

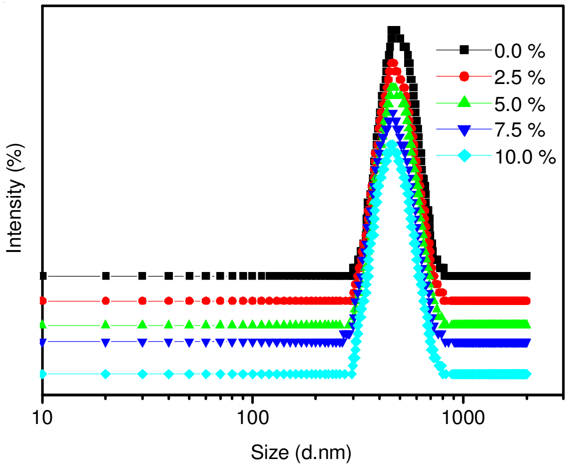

Fig. 2. Distribution of particle size of the latex by DLS

TABLE-7
EFFECT OF CONTENT OF SiO_2 ON THE PARTICLE SIZE OF THE LATEX AND ITS DISTRIBUTION

Content of SiO_2	Average particle size	Distribution coefficient	Distribution
0.0 %	487	0.215	200-800
2.5 %	468	0.113	200-800
5.0 %	476	0.071	200-800
7.5 %	452	0.057	200-800
10.0 %	458	0.015	200-800

Effect of silicon content on the water resistance of the coating: The tests of water absorption of the emulsion with silicon content of 0.0, 5.0 and 10.0 % were done. As can be found from Fig. 3, the film absorbed water gradually and eventually reached equilibrium in the soaking process. Nanosilica can be used as an emulsifier to stabilize polymerization process of the emulsion and can avoid some hydrophilic emulsifiers to bring about adverse effects on water resistance of the coating. Therefore, water absorption of the coating was decreased obviously. With the increase of the content of nanosized silica, the water resistance was improved significantly because the nanoparticles filled the gap in the polymer being formed to made the film more compact. Furthermore, the silica

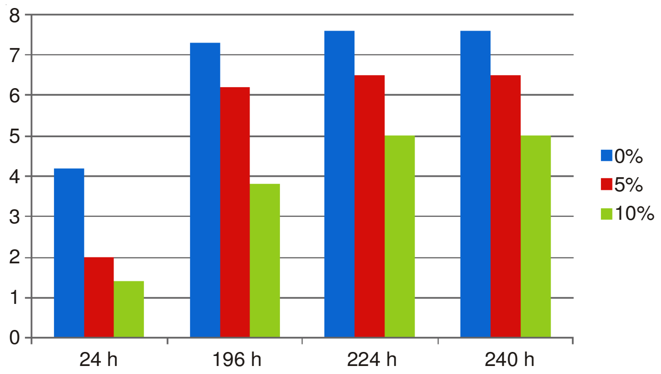

Fig. 3. Change of water absorption with time (contents of SiO_2 were 0.0 %, 5.0 and 10.0 %, respectively)

was more hydrophobic itself than polymer also to lead to improvement of the water resistance.

Effect of silicon content on glass transition temperature of SiO_2/polyacrylate coating: The glass transition temperature (T_g) of the polymer is an important parameter of structural change of the molecular chain, closely related to the properties of the materials. In the preparation process of the coating, it usually hopes that hardness of the coating would be high and also temperature of the film-forming would be low. However, in generally, the higher is the T_g and the higher are mechanical strength and hardness of materials, with an increased film-forming temperature. There is an obvious contradiction each other.

Fig. 4 showed that the T_g of the samples for contents of the SiO_2 being 0.0, 2.5, 5.0, 7.5 and 10.0 % were 13.71, 14.08, 14.68, 15.33 and 16.0 °C, respectively. In other words, the T_g was increased gradually with an increase of content of the inorganic component. It is due to condensation reaction among residual silicon hydroxyls on the surface of nanosized silicon sol in composite latex in the film forming process. With the evaporation of the water, Si-O-Si bond formed by condensation reaction hindered movement of the organic polymer chain segment, causing increase of the T_g. Thus, the mechanical properties of materials were improved further. Although the T_g was increased, the change is not obvious and there is little effect on the film forming temperature. Therefore, the coating added by inorganic SiO_2 were both the significantly improved mechanical performance and acceptable change of the film forming temperature. This contradiction could be ignored.

Effect of content of the silicon on the mechanical properties of the coating: It can be seen from Table-8, emulsion of polyacrylate had a very good adhesion itself. Effect of the increasing of content of nanosized silica on the level of adhesion was not obvious. However, with the increase of content of the silicon the mechanical strength of the emulsion was improved, with the elongation, increased hardness and increased wear resistance.

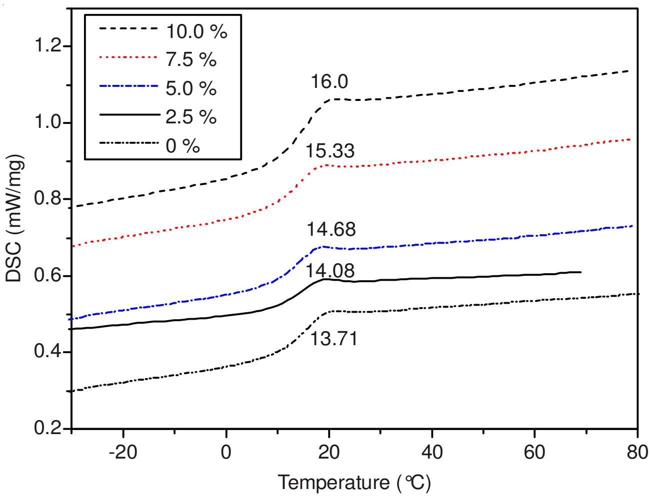

Fig. 4. DSC curves of nanosized composite latex. (Contents of the SiO_2 were 0.0, 2.5, 5.0, 7.5 and 10.0 %, respectively)

Analysis of FTIR spectroscopy: Fig. 5 presents two pieces of infrared spectra of the film with different silicon content. The spectrum with the 0 % content of SiO_2 showed methyl group band around 2957 cm^{-1} (C-H stretching), methylene group band around 2872 cm^{-1} (C-H stretching), the double peaks around 1170 and 1250 cm^{-1} (C=O symmetrical stretching of ester group) and the band around 1730 cm^{-1} (COOH stretching). However, the spectrum with the 0 % content of SiO_2 owned the sharp absorption peak around 1095 cm^{-1} corresponds to Si-O-Si anti-symmetry. At the same time, the characteristic absorption around 958 and 3450 cm^{-1} of hydroxyl groups were not observed. It indicated the occurrence of hydrolysis and condensation of Si-OH groups on the surface of SiO_2 in the film forming process. The residue of Si-OH groups in the coating was very few.

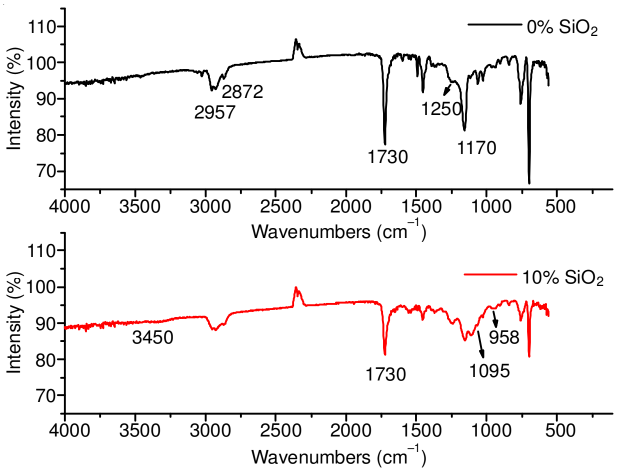

Fig. 5. Infrared spectroscopy of the film of nanosized silica-polyacrylate emulsion

TABLE-8
EFFECT OF CONTENT OF SiO_2 ON THE MECHANICAL PROPERTIES OF THE COATING

Content of SiO_2	Level of adhesion	Elongation (%)	Strength (Mpa)	Hardness	Abrasion resistance mg/10000 r 750 g
0.0 %	1	190	1.23	0.35	200
2.5 %	1	170	1.76	0.38	150
5.0 %	1	150	2.03	0.41	130
7.5 %	1	110	2.10	0.43	120
10.0 %	1	100	2.16	0.44	110

Performance of the water -based coating: The prepared acrylic paints were filmed on three different substrates in order to test its application. Figs. 6-8 showed the painted coating on the surface of woods and asbestos had no change primarily, while the surface of the iron was not well protected from the applied coating. After the iron plate being immersed in deionized water for one day, the coating surface have had some rust and rust was more severe after 10 days evenly with a slight blistering of the surface. It indicates that the coating has absorbed the deionized water in which reacted with the iron beneath the coating and resulted in a severe corrosion. Dissolution of metal caused serious consequence that the partial coating lost a capability to stick to the surface of substrate. In consequence, the partial coating separated oneself from the substrate. Its property of anti-corrosion should be improved.

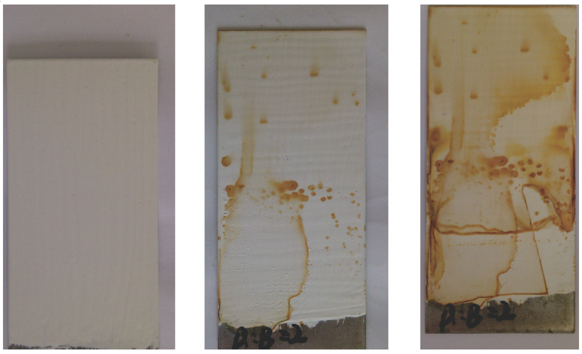

Fig. 6. Effect of the water -based coating on performance of iron plate Before experiment Soaking for 1 d in deionized water soaking for 10 d in deionized water

Fig. 7. Effect of the water-based coating on performance of wood board. Before experiment Soaking for 1 d in deionized water Soaking for 10 d in deionized water

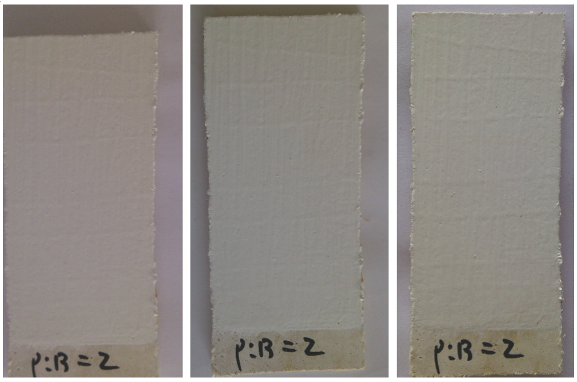

Fig. 8. Effect of the water-based coating on performance of asbestos board. Before experiment Soaking for 1 d in deionized water Soaking for 10 d in deionized water

It can be concluded that the prepared paint of nanosized silica/acrylic acid can be used on the surface of wood and wall. As the use of metallic paint, the water absorption needs to be reduced still to adjust its performance of adhesive property.

Conclusion

Emulsion of nanosized silicon oxide-polymerized acrylic ester with high solid content was prepared by soap-free emulsion polymerization successfully, using silica sol as source of nanosized silicon oxide, of which surface modified by triethylene glycol (TEG) and water-soluble initiator (ammonium persulfate). Silica sol B was selected to prepare stable aqueous emulsion of nanosized silica-acrylate polymerization successfully. The functional monomer (acrylic acid) and silicon oxide had stabilizing effect on the polymerization process. The two effects were collaborative. By the emulsifier (COPS-1, beneath the CMC concentration) and the delayed method dropwise of monomers, an aqueous soap-free emulsion of nanosized silica-acrylate with solid's content of 50 % were prepared successfully, exceeding ordinary soap-free emulsion with that of 30 %. The content of nanosized SiO_2 has a significant effect on glass transition temperature, water resistance, abrasion resistance, mechanical strength, elongation, flexibility and impact resistance of the coating of the inorganic/organic composite, *etc*. The paint of the emulsion of nanosized silica/acrylate have good adhesion and water resistance on the surface of wood and concrete, *etc*. So it has a good prospect in the field of paint of wall and coatings of wood.

ACKNOWLEDGEMENTS

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