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(54) **Title:** AQUEOUS DISPERSION OF A MODIFIED RESIN

(57) **Abstract:** This invention relates to an aqueous dispersion of modified resin. It can be widely applied in the coating field.



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Aqueous Dispersion of a Modified Resin

Technical Field

This invention involves an aqueous dispersion of modified
5 resin. It can be widely applied in the coating field.

Technical Background

Silicone modified resins have wide applications, especially
in the coating field. They can be used in heat-resistant
10 coatings, powder coatings, weather-resistant protective
coatings, H level insulation paints, sealing coatings for
electronic components, impregnated glass cloths, glass tube
coatings, wire enamel coatings and metal coil coatings.

The modification methods of silicone modified resins
15 include physical blending methods and chemical copolymerization
methods. Products obtained via the physical blending methods
are subject to the micro-phase separation, which impairs the
mechanical hardness. In chemical modifications, organic resins
are added to the backbone end or side chain of silicone through
20 condensation, free radical polymerization or addition reaction,
forming block copolymers, graft copolymers or interpenetrating
network polymers. Or the condensation reactions can happen
between the silane or siloxane containing hydroxyl groups or
alkoxy groups, and the polyester resins with low molecular
25 weight or their intermediate products containing hydroxyl
groups or alkoxy groups (with the catalysts).

Reactions between silicones and resins can occur in solution
in advance, as well as in the film formation. When using

silicone intermediates to modify other organic resins in the coating industry, the concentration of the silicone intermediates in the final products is normally around 5-80wt%. If the concentration is lower than 10wt%, the modification effect will not be so obvious. If the concentration is higher than 50wt%, the cost will be too high. The varieties of the silicone modified resins mainly include the silicone modified alkyd resins, polyester resins, polyacrylic ester, epoxy resins and polyurethane. However, the present products of the silicone modified polyester resins are mainly based on organic solvent and the concentration of solvent could be 40wt% or even more, of which the production and application process has adverse influence on environment and the health of the product line personnel.

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Invention Descriptions

This invention accidentally discovered an aqueous system of silicone modified polyester resin, which possesses multiple advantages, including a wide adjustable range of solid content, a simple production process, high stability and environment-friendliness.

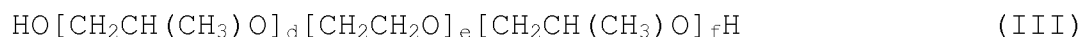
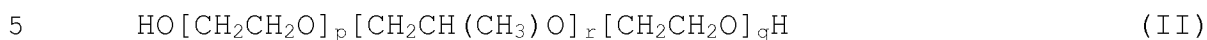
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The technical protocols to achieve the invention goals can be concluded as below:

An Aqueous system of silicone modified polyester resin containing a non-ionic surfactant with the HLB value ≥ 12 , wherein the non-ionic surfactants containing repeating ethylene oxide units and the silicone modified polyester resin being in the discontinuously oil phase.

25

The aqueous system above, wherein non-ionic surfactants are one or the combination of surfactants (I) to (IV),



wherein R_1 is a monovalent group of the formula $R(C=O)_kO-$, wherein R is a monovalent C5-C20 hydrocarbon radical, k is 0 or 1,

10 preferably R_1 is C6-C20 alkoxy or phenolic group or carboalkoxy, more preferably undecyloxy, dodecyloxy, hexadecyloxy, octadecyloxy, octadecyloxyCarbonyl, nonylphenol, octylphenol, dodecylphenol,

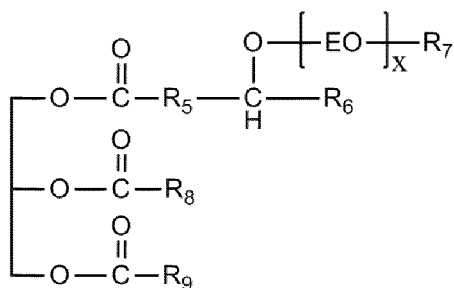
R^*_1 is a divalent group of the formula $-R^*(C=O)_lO-$, wherein

15 R^* is a divalent C5-C20 hydrocarbon radical and l is 0 or 1,

p is 0 or positive integer; m , n , q , r , d , e or f is positive integer; and $p+q>r$, $d+f<e$,

the Mn number average molecular weight of (Ia), (Ib), (II) and (III) is between 1000 and 30000 g/mol, preferably 5000 and

20 20000 g/mol,



(IV)

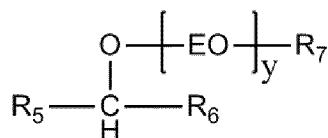
wherein R_5 is divalent C4-C24 hydrocarbon radicals, preferably C6-C20 alkylene radical, C6-C20 alkenylene radical, C6-C20 alkadienylene radical, and C6-C20 alkatetraenylene radical,

5 R_6 is monovalent C4-C24 hydrocarbon radical, preferably C6-C20 alkyl radical, C6-C20 alkenyl radical, C6-C20 alkadienyl radical, and C6-C20 alkatetraenyl radical,

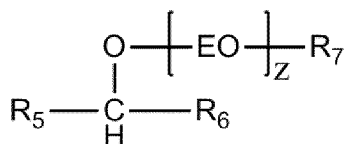
R_7 is H or C1-C3 alkyl radical, preferably H,

R_8 is C6-C20 hydrocarbyl radical, or

10



R_9 is C6-C20 hydrocarbyl radical, or



15

x, y, z is 0 or positive integer; and x, y, z should not be 0 at the same time, preferably $x+y+z \geq 36$,

-EO- is ethylene oxide unit.

20 The aqueous system above, wherein the surfactant is one or the combination selected from the group containing: copolymer of ethylene oxide and propylene oxide, polyoxyethylene stearyl ether, polyoxyethylene stearate ester, C16-C18 fatty alcohol polyoxyethylene ether, polyoxyethylene ether castor oil,
25 polyoxyethylene ether hydrogenized castor oil, nonylphenol

polyoxyethylene ether, and the HLB value of the surfactant should be ≥ 14 .

The aqueous system above, wherein the surfactant is the mixture of polyoxyethylene ether castor oil and copolymer of ethylene oxide and propylene oxide, and the HLB value of polyoxyethylene ether castor oil is ≥ 12.7 , and the HLB value of copolymer of ethylene oxide and propylene oxide is ≥ 14 .

The aqueous system above, the surfactant is the mixture of polyoxyethylene ether hydrogenized castor oil and copolymer of ethylene oxide and propylene oxide, and the HLB value of polyoxyethylene ether castor oil is ≥ 13.1 , and the HLB value of copolymer of ethylene oxide and propylene oxide is ≥ 14 .

The aqueous system above, wherein the surfactant is the mixture of polyoxyethylene ether hydrogenized castor oil and C16-C18 alcohol polyoxyethylene ether, and the HLB value of polyoxyethylene ether hydrogenized castor oil is ≥ 13.1 , and the HLB value of C16-C18 alcohol polyoxyethylene ether is ≥ 18.8 .

The aqueous system above, wherein the dosage of the non-ionic surfactant is 0.16-15 wt%, preferably 1-10 wt% based on the whole aqueous system.

The aqueous system above, wherein water is continuous phase, and the weight percent of water is 15-90 wt%, preferably 20-50 wt% based on the whole aqueous system.

The aqueous system above, wherein solid content is between 10-65 wt%, preferably 20-60wt%, and more preferably 30-55wt%.

The aqueous system above, wherein the system including emulsion or suspension, preferably emulsion, preferably Oil in

Water emulsion with particle size of 100 nm-2000 nm, more preferably 100 nm-1000 nm, wherein the span of the particle size distribution is 1.2-2.4.

The aqueous system above, wherein the acid number of
5 silicone modified polyester resin is 0.2-50 mg KOH/g, preferably 2.5-25 mg KOH/g.

The aqueous system above, wherein the silicone content is 5-80 wt% based on the silicone modified polyester, prefer 15-60wt%, more prefer 15-50wt%.

10 The aqueous system above, wherein silicone modified polyester resins are resulted from polyester resins modified by silicone intermediates containing active groups of alkoxy groups and/or hydroxyl groups.

As the aqueous system said above, which can be characterized
15 in that the oil phase is incontinuous and may contain, but not limited to esters, ketones, alkanes, alcohol ethers and/or alcohol-ether-esters and/or dibasic esters or the mixture thereof; including ethyl acetate and butyl aetate; including dibasic esters mixtures of dimethyl succinate, dimethyl
20 glutarate and dimethyl adipate; including acetone, butanone, cyclohexanone; including aromatic hydrocarbons, butyl cellosolve, butyl alcohol; including alcohol-ether-esters of ethylene glycol series, alcohol-ether-esters of propylene glycol series; preferably including ethylene glycol monobutyl
25 ether acetate, propylene glycol monomethyl ether acetate, propylene glycol methyl ether propionate, di(propylene glycol) methyl ether acetate, ethylene glycol monoethyl ether acetate,

di(2-ethoxyethoxy)ethyl acetate, 2-butoxyethyl acetate and di(2-butoxyethoxy)ethyl acetate.

The products of the silicone modified polyester resins could be either solid or liquid. The solid silicone modified polyester resins should be dissolved in the solvents in advance, forming even phase solution. Normally, high concentration solution with less solvent is preferred.

Add the silicone modified polyester resin solution and appropriate amount of nonionic emulsifiers into the reaction kettle, mix well by stirring under the room temperature, add water into the reaction kettle while stirring, add appropriate amount of preservatives, and the aqueous system in this invention is obtained. In some conditions, appropriate amount of water should be added to the mixture of the silicone modified polyester resin solution and nonionic emulsifiers during their mixing stage.

The solid content of the aqueous system in this invention is characterized in that measure 2 ± 0.2 g of sample into the petri dish with the diameter of 75 mm, desiccate for 30 minutes at the temperature of 150 ± 2 °C and the solid content is the weight ratio of the obtained solid materials compared to the initial aqueous system.

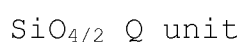
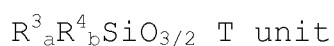
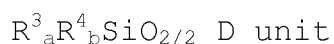
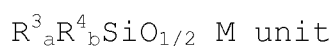
The aqueous system in this invention should meet the stability requirement of: in the 6-month static storage period under the room temperature, simple mechanical stirring could re-disperse it to the fluids suitable for industrial production.

A Preferred emulsion from the invention aqueous system meets the stability requirement of: in the 2weeks static storage period under 50°C, the emulsion is not breaking, wherein the diameter of the emulsion is 100nm-2000nm; prefer 100nm-1000nm
5 with span of 1.2-2.4.

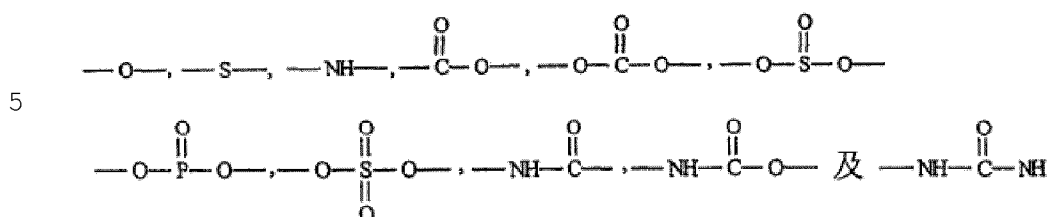
The silicone modified polyester resins are the reaction products of the polyester resins or polyester intermediates containing alkoxy groups and/or hydroxyl groups, and the intermediate products of silicone containing alkoxy groups
10 and/or hydroxyl groups, with or without using catalysts. This reaction is the co-condensation method well known by technicians in this field. As for typical preparation method, please refer to the content on the polyesters modified silicone resins in Chapter 8.4.2 of "Synthesis Technology and Products
15 Application of Silicone Products" by Guoqiao Lai, Songmin Xing, Chemical Industry Press, May 2010, Second Edition.

The acidic values of the silicone modified polyester resins suitable for this invention should be 0.2-50 mgKOH/g, preferably 2.5-25 mgKOH/g.

20 The preferred silicone intermediates for modification are those containing silanol group (containing the functional group of Si-OH) and/or Si-alkoxy group (containing the functional group of Si-OR), including one or more of M unit, D unit, T unit and Q unit.



R^3 and R^4 represents carbon-hydrogen groups of C1- C20, respectively, optionally mixed with heteroatom linking groups, including but not limited to:



a is an integer among 0, 1, 2 or 3, preferably 0, 1 or 2;

b is an integer among 0, 1, 2 or 3, preferably 0, 1 or 2;

10 In M unit, $a+b=3$,

in D unit, $a+b=2$, and

in T unit, $a+b=1$.

R^3 and R^4 represents preferably alkyl group of C1- C18, aryl group of C6- C20, aryl alkyl group of C7- C18, cycloalkyl group of C5- C12, C2- C18 alkenyl group, diol group, epoxy group (the oxygen atoms don't connect directly to the silicon atoms), alkoxy group of C1- C18, unsaturated alkyl group of C2- C20 (like vinyl, allyl, propenyl, isopropenyl group), and the terminal C4- C18 groups of alkenyl, alkynyl, and vinyl ether and allyl ether group. More preferably, R^3 , R^4 represents methyl, ethyl, vinyl, allyl, methoxy, and ethoxy and phenyl group, respectively.

15

20

The molecule may contain or form silsesquioxane and poly-phenyl silsesquioxane and/or poly-methyl silsesquioxane, which consist of T units.

25

These intermediate products of silicone can be terminated by regular terminal groups, such as one or more of trialkylsilyl,

dialkylsilanol, dialkylalkoxysilyl, alkyl dialkoxysilyl, trialkoxysilyl, dialkylvinylsilyl, triaryl silyl, diarylsilanol, diarylalkoxysilyl, aryl dialkoxysilyl, diarylvinylsilyl.

5 The preferred of silicone intermediates are methoxy phenyl /methyl silicone resins, among which the mole ratio of phenyl vs. (methoxy and alkyl) is (0.5-2):1, preferably (0.5-1.5):1, even more preferably (0.8-1.2):1. The phenyl content in the resin is 20-50wt%.

10 The silicone intermediates could be the liquid or solid silicone resins under the room temperature. The commercial silicone resins suitable for this invention include: SILRES® SY 231, SILRES® SY300, SILRES® IC 232, SILRES® IC 368, SILRES® IC 678, SILRES® IC 836, Shin-Etsu KR211, KR212, KR214, KR216, Dow
15 Corning Z 6018, Dow Corning 3037, Dow Corning 233, Dow Corning 249 or Dow Corning 3074.

In the silicone intermediates, the alkoxy groups are normally 15-18 wt% of the intermediates and the hydroxyl groups are normally 3-6 wt% of the intermediates. The higher content
20 of alkoxy and/or hydroxyl groups means stronger reactive activity with polyester.

The polyesters in this invention are the hetero chain macromolecular compounds with many carboxylic ester groups as their backbone components. They are different from other ester-
25 containing polymers with carboxylic ester groups as their backbone side chains, such as cellulose, polyacrylic and polyvinyl esters. The polyester resins in this invention are

preferably the polyester resins containing ester groups in both main and side chains.

The preferable polyesters in this invention can be obtained through the condensation between the dibasic or polybasic
5 carboxylic acids or their functional derivatives, and the dibasic or polybasic alcohol/phenols.

The proper polyesters can be regularly synthesized by carboxylic acids (or their acid anhydride) containing 2 or more acidic functional groups, and alcohols containing 2 or more
10 hydroxyl functional groups. The examples of the proper carboxylic acids (anhydride) containing multiple functional groups include: succinic acid (anhydride), glutaric acid (anhydride), benzene-1,2,4-tricarboxylic acid, phthalic acid (anhydride), tetrahydrophthalic acid (anhydride),
15 hexahydrophthalic acid (anhydride), inner bicycle-2,2,1-5-enanthine-2,3-dicarboxylic acid, tetrachlorophthalic acid (anhydride), cyclohexanedicarboxylic acid, isophthalic acid, terephthalic acid, azelaic acid, maleic acid (anhydride), trimesic acid, 3,6-dichlorophthalic acid, tetrachlorophthalic
20 acid, adipic acid and sebacic acid. The examples of the proper alcohols containing multiple functional groups include: glycerol, trimethylol propane, pentaerythritol, ethylene glycol, diethylene glycol, propanediol, 1,3-propylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, heptanediol,
25 hexanediol, octanediol, 2-butyl-2-ethyl-1,3-propanediol, neopentyl glycol, trimethyl pentanediol, Cyclohexanedimethanol.

It depends on the mole ratio of -COOH/-OH in monomers mixture whether the polyester mainly contains carboxylic acid

functional groups of -COOH or hydroxyl functional groups of -OH. In most cases, polyester suitable for this invention are basically the straight chains with 2 or more hydroxyl or carboxylic acid functional groups, or the side chains with more than 2.5 hydroxyl or carboxylic acid functional groups. Under more cases, the polyesters with various structural units are suitable.

Examples:

Without specific instructions, all percentages in this invention are based on weight to weight.

Genapol X1005, provided by Clariant. It is polyoxyethylene stearyl ether, which contains 100 EO groups in one molecule. The HLB value is 19. It is used as surfactant directly.

Emulsogen EL 360, provided by Clariant. It is polyoxyethylene ether castor oil, which contains 36 EO groups in one molecule. The HLB value is 12.7. It is used as surfactant directly.

Eumulgin HPS, provided by Cognis. It is polyoxyethylene ether hydrogenized castor oil, which contains 40 EO groups in one molecule. The HLB value is 13.1. It is used as surfactant directly.

Pluronic F127, provided by BASF. It is block copolymers based on ethylene oxide and propylene oxide. The HLB value is 14. It is used as 10wt% water solution.

Myrj S100, provided by Croda. It is polyoxyethylene stearate ester which contains 100 EO groups. The HLB value is 18.8. It is used as 10wt% water solution.

Brij S100, provided by Croda. It is polyoxyethylene stearyl ether which contains 100 EO groups. The HLB value is 19. It is used as 10wt% water solution.

5 EMULDAC AS 80, provided by Sasol. It is a linear C16-C18-alcohol polyoxyethylene ether containing 80 EO groups in one molecular. The HLB value is 18.8. It is used as surfactant directly.

ETOCAS 200-SO-(MV), provided by Croda. It is polyoxyethylene ether castor oil, which contains 200 EO groups in one molecule.
10 The HLB value is 18. It is used as 50wt% water solution.

Aduxol HRIC-0200, provided by Schärer & Schläpfer AG. It is hydrogenated polyoxyethylene ether castor oil, which contains 200 EO groups in one molecule. The HLB value is 18.1. It is used as 50wt% water solution.

15 NPE-50, provided by Sasol. It is ethoxylated nonylphenol, containing 50 EO groups in one molecule. The HLB value is 18.2. It is used as 50wt% water solution.

JY7200, provided by Dongguan Junyi Chemicals Tech Co, the content of methoxy phenyl /methyl silicone is 40wt% based on
20 the silicone modified polyester. This product is silicone modified polyester solution, the solid content of which is 60wt%. Propylene Glycol Monomethyl Acetate (PMA) is used as solvent. Monomers for the synthesis of polyester part are trimethylolpropane, m-phthalic acid, phthalic anhydride and
25 neopentyl glycol. Its acid value is <8 mg KOH/g.

JY7220, provided by Dongguan Junyi Chemicals Tech Co, the content of methoxy phenyl /methyl silicone is 20wt% based on the silicone modified polyester. This product is silicone

modified polyester solution, the solid content of which is 60wt%. PMA is used as solvent. Monomers for the synthesis of polyester part are trimethylolpropane, m-phthalic acid, phthalic anhydride and neopentyl glycol. Its acid value is <8
5 mg KOH/g.

Silicone modified polyester resin A (SMP A) is provided by Eternal Chemical. The content of methoxy methyl/phenyl modified silicone is 30wt% based on the silicone modified polyester. This product is silicone modified polyester solution, solid
10 content of which is 75wt%. PMA is used as solvent. Raw materials for the synthesis of polyester part of SMP A are: neopentyl glycol, 2-Butyl-2-ethyl-1,3-propanediol, phthalic anhydride, isophthalic acid, and terephthalic acid. The acid value of SMP A is 2.9 mg KOH/g, and the hydroxyl value is 25-
15 500 mgKOH/g. Molecular weight M_w is between 15000 and 17000, M_w/M_n is 6, obtained by GPC test while using polystyrene standard and THF solvent.

Silicone modified polyester resin B (SMP B) is provided by Eternal Chemical. The content of methoxy methyl/phenyl modified
20 silicone is 15wt% based on the silicone modified polyester. This product is silicone modified polyester solution, solid content of which is 60wt%. PMA, butyl alcohol and butyl cellosolve are used as solvents. Raw materials for the synthesis of polyester part of SMP B are: neopentyl glycol,
25 terephthalic acid, and phthalic anhydride. The acid value of SMP B is lower than 10 mg KOH/g.

MBS is isothiazolinone type preservative, provided by Thor Company.

The surfactant hydrophilicity is shown as HLB value, i.e. Hydrophilic Lipophilic Balance, in this invention. The calculation formula of HLB value is:

HLB value of nonionic surfactant = (mole weight of hydrophilic
5 part / mole weight of surfactant) × (100/5)

Table 1

Raw material	example 1	example 2	example 3	example 4	example 5	example 6	example 7
SMP A (75% solid content)	53.3	65	65	52	52	52	52
Genapol X1005							10
Emulsogen EL360						10	
Myrj S100 (10% water solution)					10		
Brij S100 (10% water solution)				10			
PLURONIC F127 (10% water solution)			16				
EMULDAC AS 80		5					
ETOCAS 200-SO-(MV) (50% water solution)	13.4						
MBS (biocide)	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Water	33.1	29.8	18.8	37.8	37.8	37.8	37.8
Total	100	100	100	100	100	100	100
Particle size D50/ μ m	0.61	0.46	0.79	0.88	0.82	47.13	0.13

The solid contents in examples 1-7 are within the range of 40-50wt%.

The process is: put surfactants and SMP A solution into the vessel, stir until uniform, and water is added into the vessel
5 step by step along with stirring. Then preservative is added into the vessel. The particle sizes of the emulsion examples 1-7 are listed in the Table 1.

In order to decrease the solvent content in the final emulsion, solvent would be evaporated at the beginning: Put the
10 SMP A solution into the vessel, vacuum the vessel under certain temperature and stirring. After certain time, the concentrated SMP A solution is added to the vessel with surfactant(s) along with stirring. When the system becomes homogenous, add water and preservative to the vessel step by step. Emulsion with
15 lower solvent content and higher non-volatile content could be prepared by this way.

Table 2

Raw material	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13
SMP A (75% solid content)	53.3	52	52	52	52	52
Eumulgin HPS					1.6	
Emulsogen EL360						4
ETOCAS 200-SO- (MV) (50% water solution)	3.2	2		8		
EMULDAC AS 80		2	2			
Myrj S100 (10% water solution)						
Brij S100 (10% water solution)				8		
PLURONIC F127 (10% water solution)	12.8		6.4		6.4	8
MBS	0.2	0.2	0.2	0.2	0.2	0.2
Water	30.5	43.8	39.4	31.8	39.8	35.8
Total	100	100	100	100	100	100
Particle size D50/ μm	0.48	0.77	0.69	0.54	0.53	\

Table 3

Raw material	Example 14	Example 15	Example 16
JY7200 (60% solid content)	52		
JY7220 (60% solid content)		52	
SMP B (60% solid content)			52
PLURONIC F127 (10% water solution)	12.8	12.8	9.6
ETOCAS 200-SO-(MV) (50% water solution)	3.2	3.2	4.8
MBS	0.2	0.2	0.2
Water	31.8	31.8	33.4
Total	100	100	100
Particle size D50/ μm	0.61	0.48	0.43

Table 4

Raw material	Example 17	Example 18
SMP A (75% solid content)	52	52
NPE-50 (50% water solution)	16	\
Aduxol HRIC-0200 (50% water solution)	\	4
PLURONIC F127 (20% water solution)	\	7
MBS	0.2	0.2
Water	31.8	36.8
Total	100	100
Particle Size D50/ μm	0.19	0.52

The process is: put surfactants and silicone modified polyester solution (including SMP A, SMP B, JY7200、JY7220) into the vessel, stir until uniform, and the water is added into the vessel step by step along with stirring. Then
5 preservative is added into the vessel. White emulsion products are obtained. The particle sizes of the emulsion examples are listed in above Tables. The emulsion product prepared by example 13 is a little break up after storing one week at 50°C. But it could be re-dispersed to fluids suitable for industrial
10 production by simple mechanical stirring and meets the stability requirement in this invention.

The solid contents in O/W emulsion examples 8-18 are within the range of 30-50wt%.

Under the room temperature, evenly coat the product of each
15 embodiment example with 80- μ m wire bar coaters on experimental aluminum plates (A-36) provided by Q-Lab. The dried coating thickness is about 20-30 μ m (dry the film after curing and the curing condition is 150°C for 15 minutes).

Measure the gloss degree using the gloss meter and observe
20 the yellowing degree, obtaining the test data as below:

Table 5

Sample name	Control sample*	Embodiment Example 1	Embodiment Example 2	Embodiment Example 3	Embodiment Example 4	Embodiment Example 12	Embodiment Example 13	Embodiment Example 14
Initial gloss	118.9	127.2	132.6	126	71.9	82.1	79.9	82.1
200°C/1h	Yellow	Yellow	Colorless transparent	Colorless transparent	Colorless transparent	Colorless transparent	Colorless transparent	Yellowish
Gloss 1	111.1	123.8	122.7	132.7	74.1	85.7	83.0	87.3
250°C/1h	Deep yellow	Yellowish	Yellow	Colorless transparent	Yellow	Yellowish	Yellow	Yellow
Gloss 2	96.1	117.6	123.6	115.7	70.30	87.83	81.07	84.83

*Control sample is an oil-in-water emulsion prepared with 0.96% PVA 2588 (PVA2588, the viscosity of 4% water solution is 25 mPa•s according to DIN53015 at 20°C and the alcoholysis degree of PVA is 88%, 10wt% water solution prepared before use), 52% SMP A and 0.1% Kathon IxE preservative and water.

Based on the test data above, the embodiment examples of this invention are better than the control example using PVA as dispersant in the performance of yellowing resistance.

The particle diameter measurement used in this invention is
5 Malvern Mastersizer 2000.

The particle diameter in this invention is obtained according to the laser diffraction spectroscopy. The volume based particle diameter is based on following formula (p=4, q=3)

$$10 \quad x(p, q) = x(4, 3) = \left(\sum_{i=1}^m n_i \bar{x}_i^3 \cdot \bar{x}_i \right) / \left(\sum_{i=1}^m n_i \bar{x}_i^3 \right)$$

The span of the particle size distribution in this invention is defined as (D90-D10)/D50.

D50 is defined as the value of the particle diameter at 50%
15 in the cumulative distribution. For example, if D50=0.68 μm, then 50% of the particles in the sample are larger than 0.68 μm, and 50% smaller than 0.68 μm. D10 or D90 is defined as the value of the particle diameter at 10% or 90% in the cumulative distribution respectively. For example, if D10=0.1 μm, then 10%
20 of the particles in the sample are smaller than 0.1μm, if D90=1 μm, then 90% of the particles in the sample are smaller than 1μm.

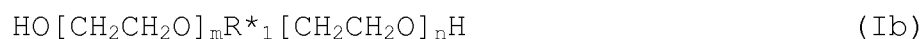
The hardness test instrument used in this invention is "Scratch Hardness Tester Model 291" manufactured by Erichsen
25 and the hardness is measured according to the Standard of ISO15184. The gloss meter used in this invention is "LZM151" manufactured by Erichsen and the gloss is measured according to the Standard of ISO2813. The data listed in the table are the

measurement results at 60°. The colorimeter used in this invention is "Color Guide 45/0" manufactured by BYK Gardner and the measurement is based on the Standard of GB/T11186.1-89.

Claims

1. An Aqueous system of silicone modified polyester resin containing a non-ionic surfactant with the HLB value ≥ 12 , wherein the non-ionic surfactants containing repeating ethylene oxide units and the silicone modified polyester resin being in the discontinuously oil phase.

2. The aqueous system according to claim 1, wherein non-ionic surfactants are one or the combination of surfactants (I) to (IV),



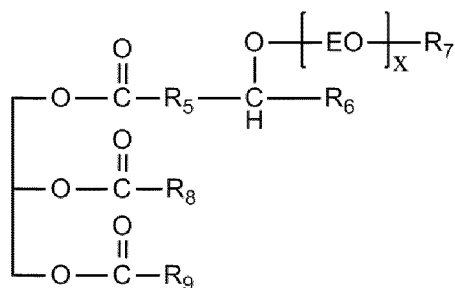
wherein R_1 is a monovalent group of the formula $R(C=O)_kO-$, wherein R is a monovalent C5-C20 hydrocarbon radical, k is 0 or 1,

preferably R_1 is C6-C20 alkoxy or phenolic group or carboalkoxy, more preferably undecyloxy, dodecyloxy, hexadecyloxy, octadecyloxy, octadecyloxyCarbonyl, nonylphenol, octylphenol, dodecylphenol,

R^*_1 is a divalent group of the formula $-R^*(C=O)_lO-$, wherein R^* is a divalent C5-C20 hydrocarbon radical and l is 0 or 1,

p is 0 or positive integer; m , n , q , r , d , e or f is positive integer; and $p+q>r$, $d+f<e$,

the Mn number average molecular weight of (Ia), (Ib), (II) and (III) is between 1000 and 30000 g/mol, preferably 5000 and 20000 g/mol,



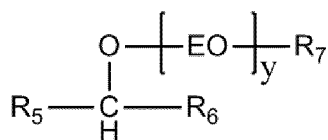
(IV)

wherein R_5 is divalent C4-C24 hydrocarbon radicals, preferably C6-C20 alkylene radical, C6-C20 alkenylene radical, C6-C20 alkadienylene radical, and C6-C20 alkatetraenylene radical,

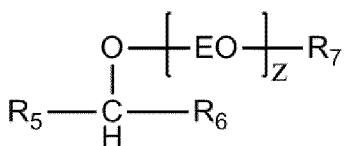
R_6 is monovalent C4-C24 hydrocarbon radical, preferably C6-C20 alkyl radical, C6-C20 alkenyl radical, C6-C20 alkadienyl radical, and C6-C20 alkatetraenyl radical,

R_7 is H or C1-C3 alkyl radical, preferably H,

R_8 is C6-C20 hydrocarbyl radical, or



R_9 is C6-C20 hydrocarbyl, or



x, y, z is 0 or positive integer; and x, y, z should not be 0 at the same time, prefer $x+y+z \geq 36$,

-EO- is ethylene oxide unit.

3. The aqueous system according to claim 1 or 2, wherein the surfactant is one or the combination selected from the group containing: copolymer of ethylene oxide and propylene oxide, polyoxyethylene stearyl ether, polyoxyethylene stearate

ester, C16-C18 fatty alcohol polyoxyethylene ether, polyoxyethylene ether castor oil, polyoxyethylene ether hydrogenized castor oil, nonylphenol polyoxyethylene ether, and the HLB value of the surfactant should be ≥ 14 .

5

4. The aqueous system according to claim 1, wherein the surfactant is the mixture of polyoxyethylene ether castor oil and copolymer of ethylene oxide and propylene oxide, and the HLB value of polyoxyethylene ether castor oil is ≥ 12.7 , and
10 the HLB value of copolymer of ethylene oxide and propylene oxide is ≥ 14 .

5. The aqueous system according to claim 1, the surfactant is the mixture of polyoxyethylene ether hydrogenized castor oil
15 and copolymer of ethylene oxide and propylene oxide, and the HLB value of polyoxyethylene ether castor oil is ≥ 13.1 , and the HLB value of copolymer of ethylene oxide and propylene oxide is ≥ 14 .

20 6. The aqueous system according to claim 1, wherein the surfactant is the mixture of polyoxyethylene ether hydrogenized castor oil and C16-C18 alcohol polyoxyethylene ether, and the HLB value of polyoxyethylene ether hydrogenized castor oil is ≥ 13.1 , and the HLB value of C16-C18 alcohol polyoxyethylene
25 ether is ≥ 18.8 .

7. The aqueous system according to claim 1-6, wherein the dosage of the non-ionic surfactant is 0.16-15 wt%, preferably 1-10 wt% based on the whole aqueous system.

5 8. The aqueous system according to claim 1-6, wherein water is continuous phase, and the weight percent of water is 15-90 wt%, preferably 20-50 wt% based on the whole aqueous system.

10 9. The aqueous system according to claim 1-6, wherein solid content is between 10-65 wt%, preferably 20-60wt%, and more preferably 30-55wt%.

15 10. The aqueous system according to claim 1-6, wherein the system including emulsion or suspension, preferably emulsion, preferably Oil in Water emulsion with particle size of 100 nm-2000 nm, more preferably 100 nm-1000 nm, wherein the span of the particle size distribution is 1.2-2.4.

20 11. The aqueous system according to claim 1-6, wherein the acid number of silicone modified polyester resin is 0.2-50 mg KOH/g, preferably 2.5-25 mg KOH/g.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/053106

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J3/07 C08L67/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 520 466 A2 (DOW CORNING TORAY SILICONE [JP]) 30 December 1992 (1992-12-30) claim 3; example 2 -----	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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)

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"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

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"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

Date of the actual completion of the international search

7 April 2015

Date of mailing of the international search report

16/04/2015

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/053106

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0520466	A2	30-12-1992	
		DE 69202822 D1	13-07-1995
		DE 69202822 T2	16-11-1995
		EP 0520466 A2	30-12-1992
		JP H059409 A	19-01-1993
		JP 2787737 B2	20-08-1998
		US 5708057 A	13-01-1998
