



Surfactant-free latexes as binders in paint applications

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ABSTRACT

The leakage of surfactant from waterborne coatings is a matter of concern. Therefore, there is a strong interest in developing surfactant-free polymer dispersion as binders for waterborne coatings. This will accelerate the substitution of solventborne binders by the more environmentally friendly waterborne latexes. However, as the performance of the coating depends on the interaction of the latex with pigments and fillers and this interaction is controlled by the composition of the surface of the polymer particles, it is an open question if the surfactant-free latexes are adequate for coating applications. In this work, surfactant-free latexes synthesized under industrial-like conditions using sodium styrene sulfonate (NaSS) to provide stability to the latex were used to formulate exterior paints and their performance compared with that of a commercial latex binder. It was found that for most of the application properties, the paints based on the NaSS binders present improvements with respect to the surfactant stabilized commercial binder.

1. Introduction

Coatings are ubiquitous materials that have a strong economic impact. Thus, the estimated cost of corrosion is 3.4% of the global gross domestic product (GDP, data from 2013) [1]. Although apparently simple, coatings are very complex hybrid materials. The coating industry is undergoing a profound transformation because waterborne polymer dispersions (latexes) are replacing solventborne polymers in the coatings market due to the combined push of environmental regulation and customers preferences. However, the substitution in demanding applications is not simple because the quality of the films formed from waterborne systems is affected by the intrinsic characteristics of the latexes. Thus, latexes are formed by individual polymer particles that during the film formation process, they come in contact upon water evaporation, deform under the action of the interfacial tensions and in order to form a good film interpenetration of polymer chains between adjacent particles is desired. Interpenetration can be facilitated by lowering the glass transition temperature (T_g) of the polymer, but this leads to poor mechanical properties. The need of combining easy film forming with good mechanical properties is sometimes referred as the film formation paradox [2]. The traditional way of overcoming this problem involves the use of a solvent (coalescent agent) that reduces the effective T_g during film formation. Later, the

solvent evaporates releasing volatile organic compounds. As environmental regulations have imposed severe restrictions to the use of coalescent agents, multiphase polymer particles [3–8] and crosslinking using covalent [9–12], ionic [13], and hydrogen [14,15] bonds are used to overcome the film formation paradox.

Although the film formation paradox is an important drawback of the waterborne polymer dispersions, it is not the only one. Latexes are thermodynamically unstable and stability is commonly provided by surfactants, which have been qualified as necessary evil [16] because they are needed for polymer particle nucleation and stabilization, but during film formation they desorb from the particles and migrate through the film reducing gloss and adhesion and increasing water sensitivity [2]. Surfactants can also leach to the environment.

A way of avoiding surfactant migration is to attach it covalently to the polymer by using reactive surfactants (surfmers) [10,17]. The main difficulty using surfmers is that the surfmer should be reactive enough to be fully incorporated at the end of the process and not too reactive to avoid burying during the semicontinuous process [18]. As this balance depends on the reactivity ratio between the surfmer and the monomers in the formulation, a change in the monomer system forces to either change the surfmer or the way in which the surfmer is used, which limits the general applicability of the surfmers.

Another possibility is to employ monomers containing hydrophilic

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functionalities that can provide colloidal stability to the polymer particles. Monomers containing carboxylate [19], sulfonate [20], or amino [21] groups have been employed, but the sulfonate group is the most promising as it is stable and the pKa is that low that its charge remains unaffected in a broad range of pH.

We have explored the use of sodium styrene sulfonate (NaSS) to obtain high-solids surfactant-free latexes. This is challenging as NaSS is completely water-soluble and its concentration in the organic phase is virtually zero. Investigation of the fundamentals of chemical incorporation of ionic monomers in polymer colloids [22] paved the way towards the synthesis of surfactant-free waterborne polymer dispersions under industrial-like semicontinuous conditions with solids contents in the upper range of commercial latexes (from 50 wt% to 64 wt%). A modest concentration of NaSS (1.35 wt% based on monomers) was used and a high incorporation of NaSS (83.5%) was achieved [23,24]. The versatility of the approach was demonstrated by producing latexes from variety of monomers (acrylates, methacrylates, styrene) [24].

These latexes showed good colloidal stability and film forming properties. Furthermore, in films cast from pure latexes, comparison with latexes stabilized by conventional surfactant (sodium dodecyl sulfate) it was found that surfactant migration was avoided when the NaSS stabilized latexes were used [23].

However, all the tests were carried out using pure latexes, whereas coatings are multicomponent hybrid materials. In addition to the polymer latex (called binder in the coatings industry) paints contain many other components such as dispersants, wetting agents, defoamers, pigments, fillers, thickeners and biocides. Furthermore, many different and often conflicting application properties should be met. The performance of the coating is strongly affected by the interaction between the components of the formulation, in particular that of the polymer particles, with pigments and fillers. As this interaction is largely controlled by the composition of the surface of the polymer particles, it is an open question if the surfactant-free latexes stabilized with NaSS are adequate for coating applications. Therefore, in this article the performance of NaSS stabilized latexes as binders in all-acrylics exterior coatings was assessed and compared with that of a commercial latex.

2. Experimental

2.1. Materials

Technical grade methyl methacrylate (MMA, Evonik Germany), n-butyl acrylate (BA, BASF Petronas), tert-butyl hydroperoxide (TBHP, 70 wt% aqueous solution, Arkema), hydrogen peroxide (HPO, 30 wt% aqueous solution, May Chemical), potassium persulfate (KPS, Evonik), sodium p-styrene sulfonate (NaSS, purity $\geq 90\%$, Sigma Aldrich), ascorbic acid (AsAc, reagent grade, Sigma Aldrich) were used as received. In all reactions, distilled water was utilized.

For the paint formulation, thickener (Natrosol™ 250 HBR, Ashland), dispersant (Dispex™ N40, BASF), wetting agent (Hydrolat® 1080, BASF), antifoam (Foamaster® 111, BASF), pH adjuster (AMP-95™, Dow Chemical), in-can preservative (Acticide® MV, Thor), co-solvent (propylene glycol), pigment (Tioxide® TR-92, Huntsman), filler (CaCO₃ 600 mesh), associative thickener (Rheolate® 644, polyetherurea polyurethane, Elementis), coalescing solvent (Optifilm™ enhancer 300, Eastman), and dry film preservative (Acticide® EPW, Thor) were utilized. A commercial latex of undisclosed characteristics was provided by Synthomer and used for comparison.

2.2. Latex preparation

50 wt% solids content latexes stabilized with different concentrations of NaSS (0.5 wt%, 0.76 wt%, 1.0 wt%, 1.3 wt% and 3.6 wt%) were synthesized by seeded semicontinuous emulsion polymerization using TBHP/AsAc as redox initiator. A latex provided by Synthomer which is referred as Syn-A was selected for comparison purposes. Syn-A had a

glass transition temperature (T_g) similar to that of the NaSS containing latexes. As the particle size of Syn-A (150 nm) was smaller than those of the latexes stabilized with NaSS (240–310 nm), a latex comprising smaller particles was prepared. KPS was used in the seed formation and the amount of NaSS was adjusted so that the total charge contribution of KPS and NaSS in the final latex was equal to the charge of the latex with 1.3% NaSS. The solids content of this latex was 45 wt%. Details about the synthesis of these latexes are given in Supporting Information.

2.3. Preparation of paints

The waterborne paints were prepared by using an exterior formulation with 45% pigment-volume concentration (PVC). First, the millbase was prepared. The goal is to achieve a good dispersion of pigments and fillers. Then, at the letdown stage, the millbase was mixed with the binder dispersion and other additives.

The recipe of the millbase is given in Table 1 together with the specific function of each constituent. Water (85% of the total amount), dispersant, wetting agent, antifoam, buffer, co-solvent and in-can preservative were weighed and placed in a 10 L jacketed cylindrical tank and stirred by using a high speed disperser at 500 rpm for 20 min. Then, titanium dioxide (pigment) and CaCO₃ (filler) were added slowly and the stirring rate increased to 2000 rpm. After mixing for 20 min, the thickener and the rest of the water (15%) were added slowly. The whole dispersion was mixed for another 30 min to ensure homogeneity of the system. The final quality check was made by using a Hegman gauge to determine the fineness of the grind. The common requirement is to be below 40 μm , which was the case for the prepared millbase.

The next stage in paint preparation is letdown in which the millbase is blended with the binder (latex) and other ingredients (Table 2). As the latexes Syn-A and Smallsize have different solids contents than the rest of the latexes, the amount of latex and water in the formulation was different.

The pH of the binders was adjusted to 9–9.5 and the binder, coalescing solvent, dry film preservative, antifoam and 90% of the water were added to the millbase under agitation. Thickener was added to adjust the viscosities of the paints to 89–99 KU (Krebs units).

The total solids content and the PVC of the paints were held constant since the solids content determines the dry film thickness (that in turn affects durability, permeability, etc.) and the PVC which affects opacity (hiding power), durability, scrub resistance, and gloss [25]. In addition, as the latexes had different minimum film forming temperature (MFFT, Table 3), the amount of coalescing agent added was adjusted to achieve a MFFT of 5 °C, which is a common standard for paints. Thus, while 2.5 wt% (based on binder solid) was enough for NaSS containing latexes, 5 wt% was utilized for Syn-A.

2.4. Characterization methods

A detailed characterization of both latexes and paints was carried out. As the number of characterization tests is high, in order to facilitate the readability of the article, here, the different methods are

Table 1
Millbase formulation.

Ingredient	Commercial name	Amount (g)	wt%
Water		1496	29.41
Dispersant	Dispex™ N40	30.8	0.61
Wetting agent	Hydrolat® 1080	17.6	0.35
Defoamer	Foamaster® 111	17.6	0.35
pH modifier	AMP-95™	17.6	0.35
Cosolvent	Propylene Glycol	132	2.60
In-can preservative	Acticide® MV	13.2	0.26
Pigment	Tioxide® TR-92	1874.4	36.85
Filler	CaCO ₃ 600 mesh	1460.8	28.72
Thickener	Natrosol™ 250 HBR	26.4	0.52

Table 2
Letdown stage.

Ingredient	Commercial name	Amount (g)						
		3.6% NaSS	1.3% NaSS	1% NaSS	0.76% NaSS	0.5% NaSS	Small size	Syn-A
Millbase		410	410	410	410	410	410	410
Binder		226	226	226	226	226	250.26	224.86
Coalescing agent	Optifilm™ enhancer 300	2.84	2.84	2.84	2.84	2.84	2.84	5.67
Dry film preservative	Acticide® EPW	10.64	10.64	10.64	10.64	10.64	10.64	10.64
Antifoam	Foamaster® 111	0.71	0.71	0.71	0.71	0.71	0.71	0.71
pH modifier	AMP-95™	0.22	0.24	0.23	0.21	0.29	0.30	0
Thickener	Rheolate® 644 ^a	4.92	3.03	2.24	2.34	2.66	1.38	3.56
Water		54.08	55.89	56.66	56.99	56.23	33.33	54.38
Paint weight solid		54	54	54	54	54	54	54.2
Paint volume solids		35.4	35.4	35.4	35.4	35.4	35.4	35.5
Pigment volume content (PVC) %		45	45	45	45	45	45	45

^a The amount of thickener was varied to adjust the Stomer viscosity to 89–99 KU (Fig. 2).

Table 3
Characteristics of the latexes.

Code	Z-ave (nm)	Solids Content (%)	pH	Viscosity ^a (cP)	T _g (°C)	MFFT (°C)
3.6%	310	49.0	2.9	82 (1/60)	16.7	12
1.3%	250	49.2	2.7	25 (1/60)	16.9	10
1.0%	240	49.6	2.6	32 (1/60)	16.3	10
0.76%	270	48.7	2.6	24 (1/60)	15.9	10
0.5%	280	49.6	2.6	50 (1/60)	17.6	11
Smallsize	145	44.5	2.5	41 (1/60)	15.2	9
Syn-A	150	50	8.2	130 (3/60)	17.0	17

^a Brookfield. The first number in parenthesis refers to the code of the spindle used and the second number is the spinning rate.

summarized and the details of the methods are given in Supporting Information.

2.4.1. Latex and latex films characterizations

The characteristics determined include particle size (dynamic light scattering), solids content, viscosity, specific gravity, minimum film forming temperature (MFFT), water blanching (formation of a whitish haze caused by water absorption), glass transition temperature (T_g), volatile organic compounds (VOC) content. Details of these tests are given in Supporting Information.

2.4.2. Paint characterizations

A coating should meet many widely different and sometimes conflicting requirements and therefore the complete characterization of the paint involves quite a few tests.

Viscosity is important for handling and applying the paint and these operations involve different rheological conditions. Therefore, viscosity was determined at both low shear (Stomer viscosity, characteristic of the conditions for pouring the paint) and high shear (conditions during brushing, rolling or spraying).

Paints are transported at long distances and stored for long periods of time. Accelerated stability tests were performed to obtain information about the resistance of the paint to the conditions encountered during transport and storage, especially in hot climates. Paints can also suffer stability problems in cold climates. During freezing, water forms ice crystals increasing the concentration of particles and ions in the aqueous phase. If the particles are not well stabilized, irreversible coagulation takes place. During transport and storage, paints can suffer several freeze-thaw cycles. Therefore, freeze-thaw tests were performed.

Exterior paints are often applied to highly alkaline masonry substrates. In these substrates, water soluble compounds are transported by the effect of humidity leaching out to the wall surface and forming white deposits. This phenomenon is called efflorescence and the resistance to efflorescence is a desired property of the coatings.

Aesthetics is critical for coatings. Gloss, contrast ratio (measure of

the opacity of the coating), yellowness index (a quality flaw generally associated with dirtiness, aging and degradation) and whiteness index (white color gives an impression of being clean and fresh) are important aesthetic characteristics. Complementary information is given by the colorimetric values (*L*, *a*, *b*), where *L* is related to the lightness, *a* is the green-red axis (negative values towards green) and *b* the blue-yellow axis (negative values towards blue). Hiding power, namely the capability of covering the color of the substrate, and color retention are also sought properties.

Mechanical properties are also of great importance. Thus, a paint should adhere well to the substrate (e.g. exterior walls of buildings) and withstand scrubbing. Therefore, X-cut adhesion and scrub tests were performed. On the other hand, the paint should be flexible enough to bridge the cracks that are going to be formed in the plaster 2–3 years after construction of a new building. This should be combined with minimum dirt pick up and good waterproofing and breathability [26]. In other words, the paint should be flexible and tough at the same time. This was checked by means of tensile tests.

Blocking resistance is another important characteristic for coatings. This refers to the possibility that a coated surface (e.g. a door) sticks to another surface (e.g. the frame) when the two surfaces are put in contact under pressure.

Coatings should also have good chemical resistance. In this work, alkali resistance (cement is rather alkaline) and weather resistance (a must for exterior paints) were determined.

Details for all the paint characterization tests are given in Supporting Information.

3. Results and discussion

3.1. Latex (binder) properties

The characteristics of the latexes are displayed in Table 3. The latexes synthesized by using NaSS and nonionic initiators yielded particles with particle sizes from 240 nm – 310 nm. The latex produced with the small seed synthesized using KPS yielded particles of 145 nm. It may look surprising that the latex with 3.6% NaSS had the largest particle size. This may be due to the fact that as the concentration of NaSS increased, both the amount of soluble polymer and the ionic strength increased destabilizing the particles. The pHs of the latexes synthesized in this work were in the range 2.5–3 since no buffer was utilized in the syntheses. The pH of the reference latex (Syn-A) was higher (pH = 8). The viscosities of the latexes were low. The T_g of the latexes with NaSS were in the range 15.2–17.6 °C. The minimum film forming temperatures (MFFT) of the latexes stabilized with NaSS were in the range 8.5–11.6 °C, with a slight increase caused by the NaSS, likely due to the effect of the ionic groups (either chemically attached or physically adsorbed on the particles) in hindering particle deformation [2]. Even though the T_g was similar, the MFFT of the reference latex (Syn-A) was

higher than the rest. This was attributed to the hydroplasticization resulting from the hydrophilic sulfonate moieties [27,28].

The VOC content of the latexes used as binders in the paints is important because the amount of VOCs in coatings is restricted by environmental regulations worldwide. For example, starting from 2010, the permissible VOC limit for the waterborne paints used on exterior walls of mineral substrate has been decreased to 40 g/L in ready-to-use form (about 40,000 ppm) by European Directive 2004/42/CE. The amounts of residual monomers (MMA, BA) and by products such as tert-butanol, n-butanol and butyl acetate in the latexes are displayed in Table 4. Tert-butanol is produced by hydrogen abstraction of tert-butoxy radicals [29]. Hydrolysis of butyl acrylate yields acetic acid and n-butanol which can further react to form butyl acetate. Acetone is also a by-product however it is not quantified due to being exempt in VOCs. Table 4 shows that the VOC content of the latexes was well below that of the European Directive 2004/42/CE threshold.

Water blanching of pure latex films after 24 h is displayed in Fig. 1. The visual inspection showed that the films 3.6% and Syn-A were not resistant to water. For Syn-A, the reason is that the emulsifiers can aggregate as hydrophilic pockets and increase water sensitivity [30]. The poor resistance in the case of 3.6% can be due to the presence of an excess of water soluble polymer. The best performance was displayed by 1.3% and Smallsize, which were stabilized by the same number of anions. When the NaSS content was lowered to 0.76% or 0.5% more whitening than for 1.3% was observed. It can be due to the fact that weaker repulsive interactions between the particles may ease the plasticization effect of water leading to more whitening. The detailed observations made at certain intervals are given in Supporting Information (Table S5).

3.1.1. Properties of liquid paints

The amount of thickener used for each binder was adjusted to have a Stormer viscosity in the range of 89–99 KU. Fig. 2 presents the Stormer viscosities and the amount of thickener added in each case. The efficiency of the associative thickener employed depends on the ability of the thickener to establish bridges between particles. For that, adsorption of the hydrophobic moieties of the thickener on the polymer particles is needed. Adsorption depends on both the thickener and the characteristics of the surface of the particles. With the exception of Smallsize, for the binders stabilized with NaSS, the lower the concentration of NaSS, the higher the efficiency (lower amount of thickener was needed to achieve the desired viscosity). As these latexes had similar particle sizes, the effect was attributed to a lower adsorption of the thickener due to the higher concentration of sulfonate groups on the particle surface. The Smallsize that was prepared with 1.3 wt% of NaSS, did not follow the rule and a very low amount of thickener was used to achieve the targeted viscosity. Taking into account the size of the particles and the amount of NaSS, the surface concentration of NaSS in Smallsize should be similar to the 0.76 wt% latex. Therefore, a similar adsorption of thickener is expected. Therefore, the higher efficiency was attributed to the smaller distance between particles that made easier to establish bridges among them. For a constant solids content, the interparticle distance is directly proportional to the particle size [31]. The relatively high amount of thickener needed by the reference indicates that the surfactants present

Table 4
Volatile organic compound content (VOC) of the latexes.

Code	VOCs (ppm)				
	MMA	BA	Tert-butanol	n-butanol	Butyl acetate
3.6%	26	–	34	119	53
1.3%	27	–	40	127	55
1.0%	26	–	30	114	53
0.76%	27	–	37	120	58
0.5%	26	–	38	101	60
Smallsize	33	36	29	127	54

in this binder competed for adsorption with the thickener. It can be concluded that the NaSS stabilized binders showed a very good thickener efficiency.

The characteristics of the paints are summarized in Table 5. Total solids content (TSC) was within the expected values indicating that the paint preparation was good. Brushability was good as indicated by low cone & plate viscosity.

3.1.1.1. Storage stability. The changes in paint appearance upon storage for 2 and 4 weeks at 50 °C are given in Fig. 3. It is worth mentioning that all paints were white at the beginning. Upon storage, all paints displayed phase separation. Syn-A displayed less yellowing in comparison to NaSS containing paints. The yellowing was due to the presence of ascorbic acid in the formulations. The effect of storage on the paint characteristics are detailed in Supporting Information (Table S6). No significant change in pH was observed. Syn-A showed less yellowing. Contrast ratio retention was good for the NaSS containing latexes. Since gloss values were small, it was not possible to make a solid conclusion for gloss retention.

3.1.1.2. Freeze-thaw stability. The results of the freeze-thaw test are given in Table 6 with the inset photos of the failed paints. It can be seen that with the exception of Smallsize, paints prepared with latexes stabilized with more than 0.76% NaSS resisted the 6 freeze-thaw cycles. This is a great result as stability after 3–5 freeze-thaw cycles is accepted as good enough for most commercial paints. Reference paint Syn-A was stable up to 4th cycle. The failure of Smallsize in the first cycle might be due to insufficient particle stabilization because smaller particles had a higher total surface area, and therefore the surface concentration of NaSS groups decreased. Another reason is that in close contact, small particles tend to deform and interpenetrate more than the large particles hindering redispersion.

3.1.2. Properties of the paint films

3.1.2.1. Surface properties. The gloss is important for the visual appearance of the paints. The gloss measurements of the films cast from pure latexes stabilized with NaSS showed that they had highly glossy surfaces. However, the paints prepared displayed matt surfaces (Table S7, Supporting Information) and there was no significant difference in gloss even at 85°, where the differences should be highlighted. This is due to the high PVC (45%) content of the formulation.

The opacity of the paints was evaluated by means of the hiding power and the contrast ratio (Table 7). It can be seen that all binders except that with 0.5% NaSS were comparable to or slightly better than Syn-A.

3.1.2.2. Color development and color rub. The colorimetric values (L , a , b) of the paints were determined after addition of colorant to the paints and are given in Table 8. It can be seen that the paints stabilized with NaSS provide similar color development than the reference Syn-A. ΔE_{ab} gives the difference between unrubbed and rubbed areas of the paint and the smaller the difference the better the color rub. Although all ΔE_{ab} values are within tolerance of ± 0.5 , Table 8 shows that most of the NaSS containing paints performed better than the reference latex.

3.1.2.3. Efflorescence resistance. The results of the efflorescence resistance test are provided in Table 9. Severe salting was observed in most of the NaSS containing paints. Blistering was also seen in some of the paints. On the other hand, efflorescence resistance of Syn-A was good. For efflorescence to take place, there must be moisture and alkalinity in the masonry and also a path for moisture penetration throughout the paint film [32]. The test solution fulfills the first two requirements. Moisture passes from the film-substrate interface, migrates through the paint film cross-section and reaches the paint-air interface. As water

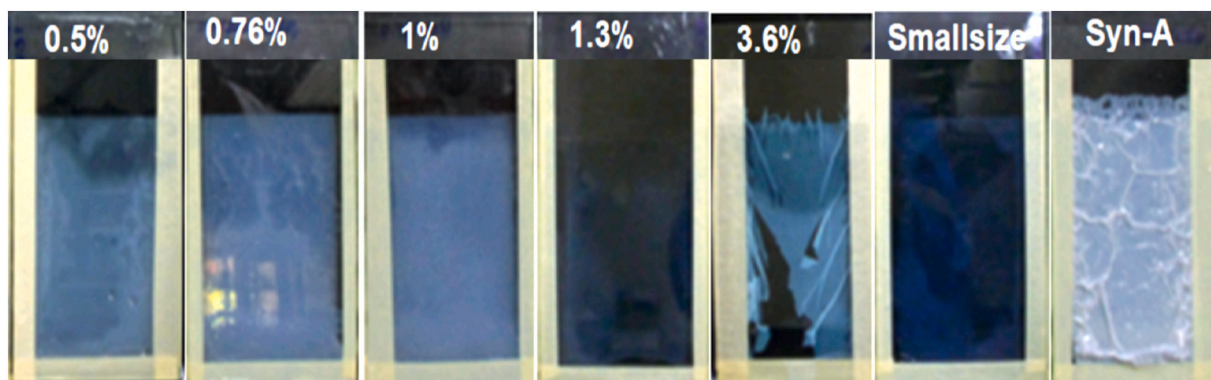


Fig. 1. Water blanching of latex films after 24 h.

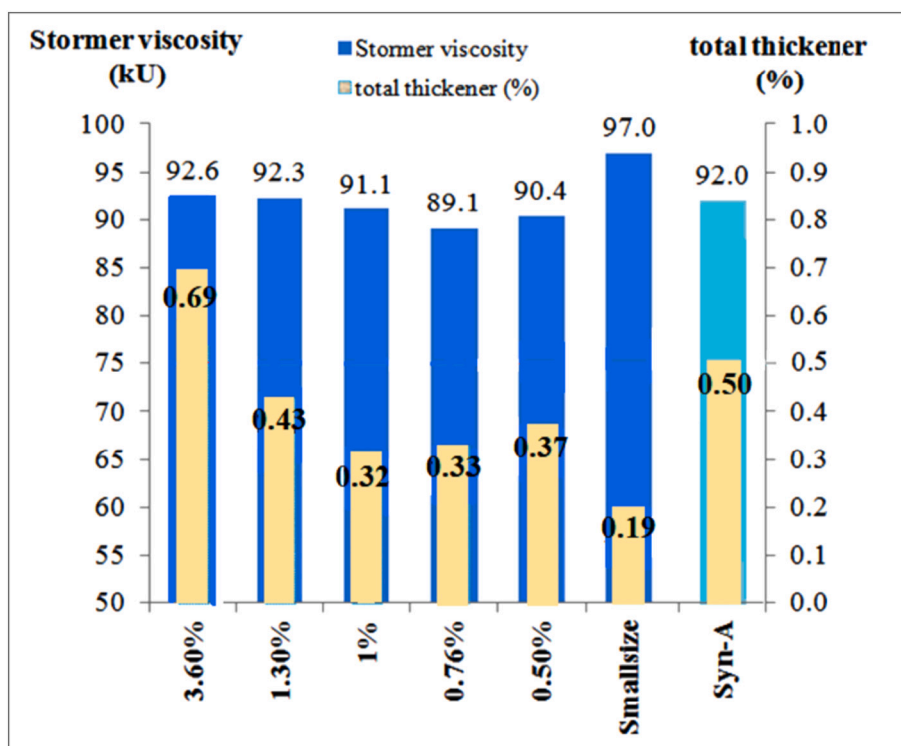


Fig. 2. Thickening response of the binders upon addition of thickener.

Table 5
Characteristics of the paints.

	3.6%	1.3%	1%	0.76%	0.5%	Smallsize	Syn-A
TSC (%)	55.0	54.9	54.6	54.5	54.8	54.8	55.3
pH	9.7	9.8	9.8	9.8	9.8	9.7	9.5
Stormer viscosity (kU)	92.6	92.3	91.1	89.1	90.4	97.0	92.0
Cone & plate viscosity (Poises)	0.40	0.45	0.50	0.35	0.30	0.45	0.35

evaporates, it leaves a dry solid behind, that is seen as solid deposits. The reason for the poor efflorescence resistance observed in NaSS containing paints can be that the NaSS groups at the surface of the particle create a path for moisture penetration. Formation of such structures has been

demonstrated in latex films from NaSS stabilized systems [23]. The formation of this kind of continuous paths that allow moisture penetration has also been found for ionic polymerizable surfactants (surfmers) [33]. On the other hand, the resistance to efflorescence of the commercial latex Syn-A was attributed to the different distribution of the hydrophilic moieties in this case. During film formation, a fraction of the surfactant migrates to the surface of the film (affecting aesthetics and adhesion) and the rest forms aggregates within the film [23]. These aggregates are not well interconnected and therefore moisture transfer is limited.

On the other hand, for the case of Syn-A, most of the emulsifier is expected to abandon the surface of the particles during film formation either migrating to the film-air interface or forming isolated aggregates of surfactant within the film [23]. Therefore, in these systems no continuous hydrophilic paths are present yielding paints with higher efflorescence resistance.

Comparison of the results of efflorescence resistance with those of blanching reported above shows that the latexes that have a good

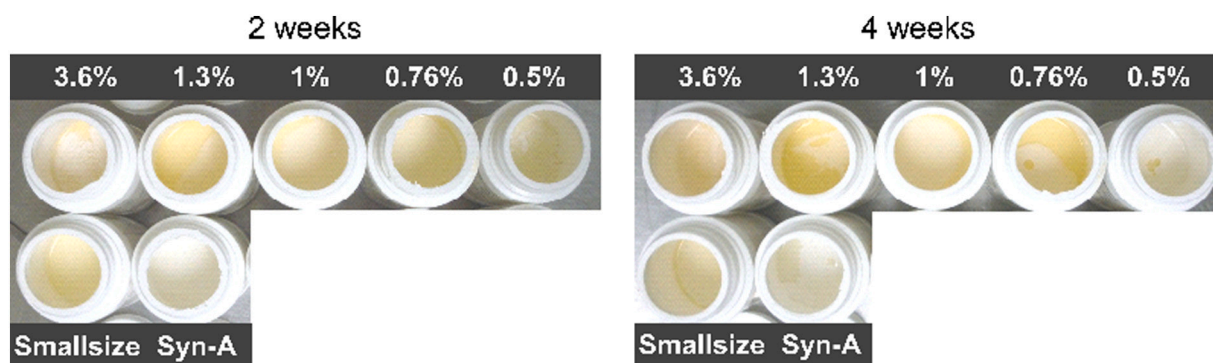


Fig. 3. The appearance of the paints upon storage for 2 and 4 weeks at 50 °C.

Table 6
Freeze-thaw stability of the paints.




	3.60%	1.30%	1%	0.76%	0.50%	Smallsize	Syn-A
1 st	✓	✓	✓	✓	viscosity inc. consistency lost 	X Gel 	✓
2 nd	✓	✓	✓	✓			✓
3 rd	✓	✓	✓	✓			✓
4 th	✓	✓	✓	✓		viscosity inc.	
5 th	✓	✓	✓	✓		X Gel	
6 th	✓	✓	✓	✓			

Table 7
Opacity of the paint films.

	3.6%	1.3%	1%	0.76%	0.5%	Smallsize	Syn-A
Contrast ratio (%)	90.7	88.4	90.5	89.1	85.7	87.8	87.5
Hiding power by appearance ^a	2	2	2	2	2	2	2

^a Visually evaluated on a scale 0–5; where 0 is poor and 5 is good coverage.

Table 8
Colorimetric values for color development and color rub tests for the colorant added paints.

	3.6%	1.3%	1%	0.76%	0.5%	Smallsize	Syn-A
L	62.9	63.0	63.2	62.8	62.8	63.3	63.1
a	0.9	1.1	1.1	1.1	1.0	0.7	0.9
b	−12.8	−12.7	-	−12.6	−12.6	−13.2	−13.3
ΔEab	0.1	0.1	0.1	0.1	0.1	0.2	0.2

blanching present poor efflorescence in paints and vice versa. As these characteristics are related to the presence of hydrophilic domains, the results may look counterintuitive, but are only the result of the different aspects that each test measures. Thus, efflorescence resistance is related

Table 9
Observations made during efflorescence resistance tests for the paints^a.

	Initial	Day 1	Day 3	Day 7
3.6%	Clear white	Slight yellowing	Salting moderate (3)	Salting severe (5), blistering
1.3%	Clear white	More yellowing	Salting mild	Salting severe (5), yellowing, blistering
1%	Clear white	Slight yellowing	Salting mild	Salting severe (4)
0.76%	Clear white	Slight yellowing	Salting mild	Salting severe (5), blistering
0.5%	Clear white	Slight yellowing	Salting moderate (3)	Salting severe (5), yellowing, blistering
Smallsize	Clear white	Slight yellowing	Salting mild	Salting severe (4)
Syn-A	Clear white	More yellowing	Salting mild	Salting mild (1)

^a Salting was evaluated in the range 0–5; where 0 is no salt and 5 is severe salting.

to transport through the film, and therefore the existence of a continuous hydrophilic path is what determines the transport. On the other hand, blanching refers to water absorption and in this case the presence of hydrophilic regions inside the film (surfactant aggregates) maximizes water absorption and therefore gives poor results in blanching. These results highlight the challenges in meeting conflicting requirements in

paints.

3.1.2.4. Mechanical properties. X-cut adhesion test results of the paints are given in Table S8 (Supporting Information). Except 0.76%, NaSS containing paints were slightly better than Syn-A, however the difference was small.

The results of the tensile tests for the paint films prepared with the different latexes are presented in Table 10. All paints were dried for 6 days at two different temperatures: 23 °C and 50 °C. It can be seen that the paints containing NaSS had higher tensile strength but less elongation at break than that with Syn-A. A possible reason is that the ionic charges of the NaSS latexes had a high binding capacity to the pigments and fillers in a way similar to that of the binders prepared with carboxylic monomers [34]. Strong adhesion of the pigment and the binder can result in less deformable paints with higher tensile strength [35]. Moreover, $\text{SO}_3^- \text{Na}^+$ groups may form ionic aggregates which act as physical crosslinks in the film, hence increasing the tensile strength. On the other hand, Table 10 shows that the mechanical properties improved when the paints were dried at higher temperature, which indicates a better film formation.

Scrub resistance is affected by many parameters such as hydrophilicity of the paint (formulation ingredients), flexibility (mechanical properties), pigment binding ability and extent of coalescence (drying time and conditions). The scrub resistance of the paints cast at 23 °C and 50 °C expressed as the maximum number of scrub cycles that the paints can withstand is presented in Table 11. It can be seen that for the NaSS containing paints, scrub resistance improved as the NaSS content decreased and for contents below 1 wt% of NaSS, the scrub resistance was better than for the reference latex. This might be a result of both lower hydrophilicity and enhanced film formation with the decrease in coalescence retardant ionic groups. The good scrub resistance obtained with the paint prepared with Smallsize (that has the same charge content than the 1.3% NaSS) also suggests that the quality of the film formation is an important parameter because coalescence of small particles is enhanced by the higher capillary pressure. The better scrub resistance observed when the paints were dried at 50 °C also support this hypothesis.

All the paints showed a good blocking resistance (Table S9, Supporting Information) in part due to the high PVC used.

3.1.2.5. Chemical and weathering resistance. Table S10 (Supporting Information) shows that the alkali resistances of all paints were comparable.

The paints exposed to natural weathering were inspected after 2 and 4 weeks. Table 12 summarizes the results of 4 weeks. The complete data are given in Table S11 of Supporting Information. Table 12 presents the variation of the lightness (L), the whiteness index (WI, Eq. S3, Supporting Information) and yellowness index (YI, Eq. S2, Supporting Information). In addition, the average sum of the differences in the colorimetric values (ΔEab) calculated using Eq. S4 (Supporting Information), which is a measure of the dirt retention is presented. The weathering results in a decrease in lightness and the whiteness index and

Table 10

Mechanical properties of the paint films dried for 6 days at different temperatures (23 °C and 50 °C).

	Tensile stress 23 °C (MPa)	Elongation at break 23 °C (%)	Tensile stress 50 °C (MPa)	Elongation at break 50 °C (%)
3.6%	3.10 ± 0.13	24 ± 4	4.74 ± 0.23	72 ± 6
1.3%	2.43 ± 0.20	88 ± 10	3.59 ± 0.10	126 ± 18
1%	1.74 ± 0.05	66 ± 4	3.00 ± 0.22	79 ± 21
0.76%	2.81 ± 0.11	61 ± 10	3.93 ± 0.24	96 ± 18
0.5%	2.16 ± 0.05	43 ± 12	3.11 ± 0.17	165 ± 35
Smallsize	2.50 ± 0.08	65 ± 20	4.54 ± 0.30	117 ± 19
Syn-A	1.43 ± 0.07	280 ± 30	2.97 ± 0.27	311 ± 69

Table 11

Scrub resistance of the paint films cast at 23 °C and 50 °C.

	3.6%	1.3%	1%	0.76%	0.5%	Smallsize	Syn-A
Max cycles 23 °C	260	610	950	1450	1400	1190	1260
Max cycles 50 °C	480	1300	1800	2400	2770	2330	2400

Table 12

Natural weathering of the paints after 4 weeks.

	3.6%	1.3%	1%	0.76%	0.5%	Smallsize	Syn-A
ΔL	-0.89	-0.62	-0.97	-0.65	-0.75	-1.38	-2.46
ΔWI	-2.32	-4.16	-3.49	-3.72	-4.59	-5.20	-9.91
ΔYI	0.35	1.01	0.56	0.83	1.23	0.76	1.71
ΔEab	0.94	0.81	1.00	0.77	0.96	1.43	2.60

an increase in yellowness. The smaller the decreases of L and WI and the increases of YI and ΔEab , the better the resistance of the paint to weathering.

Table 12 shows that the paints containing NaSS showed better natural weathering resistance than the reference paint Syn-A as they displayed less loss in lightness (ΔL) and whiteness index (ΔWI) and lower yellowness (ΔYI) and dirt retention (ΔEab) increase.

4. Conclusions

Emulsifier-free MMA/BA latexes stabilized with sodium styrene sulfonate (NaSS) were used as binders in all acrylic exterior paint formulations and their performance compared with a reference paint prepared with a conventionally stabilized commercial binder. A coating should meet many, often conflicting, application properties. A full characterization of these properties was carried out. It was found that the NaSS stabilized latexes present quite a few advantages with respect to the commercial binder. Thus, they required less thickener and show less blanching. The freeze-thaw stability, the color rub, the scrub resistance and the weathering resistance were better. The paints prepared with the NaSS stabilized binder had higher mechanical strength but less elongation at break than the commercial binder. The performance of the NaSS latexes was similar than that of the commercial paint for gloss, opacity, color development, block resistance, X-cut adhesion and alkali resistance. The only property in which the commercial latex was superior was in efflorescence resistance, where the continuous structure of the NaSS facilitates efflorescence. This work demonstrates that NaSS binders have the potential to replace surfactant stabilized latexes as binders in waterborne coatings.

CRediT authorship contribution statement

Sevilay Bilgin: Investigation, Writing- Original draft preparation; **Sobhan Bahraeian:** Methodology, Validation; **Mei Ling Liew:** Validation, Methodology; **Radmila Tomovska:** Supervision, Visualization, Writing; **José M. Asua,** Conceptualization, Supervision, writing, reviewing, editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2022.106591>.

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