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The Use of Nonionic Polymerizable Surfactants in Latexes and Paints

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Summary: In combination with anionic surfactants nonionic polymerizable surfactants lead to stable dispersions, which can be used as binders for paints. Generally the obtained results are worse than with a nonpolymerizable ethoxylated fatty alcohol. However the properties can be optimized through the right choice of the anionic surfactant. This further work is in progress.

Introduction

Emulsion polymers are often used as binders for paints, coatings, adhesives, etc. There are different ways for optimizing the properties. One possibility could be the use of polymerizable surfactants. 1959 a US-Patent mentioned the increase of the stability using polymerizable compounds with sulfonic acid groups [1]. These compounds are of anionic nature. About nonionic polymerizable surfactants there aren't so much datas in the recent literature. Ottewill and co-workers [2] investigated methoxy polyethylene glycol methacrylates in polystyrenes and found an increased electrolyte stability. This increase was only found after polymerization, blends from methoxy polyethylene glycol methacrylates with polystyrenes showed no effect. Yokota, Ichihara and Shin'ike used 1-Nonylphenoxy-2-polyoxyethylene-3-allyloxypropane to increase the water resistance of polymerfilms. Ferguson et al [4] could demonstrate, that the increase of the HLB-value from alkylethoxy acrylates increased the elecrolyte stability. Guyot and Co-workers [5] produced styrenes with hydrophobic carbonchains and hydrophilic polyethyleneoxid chains. They found, that longer polyethyleneoxid led to smaller particle sizes and better stabilities. The same researchgroup investigated also dialkyl maleates [6]. Gan et al [7] produced micro emulsions with ω-methoxy polyethyleneoxid-undecyl-α-methacrylate. Chern, Shi and Wu [8] found, comparing polymerizable NE-40 with nonpolymerizable NP-40, a larger particle size. They explained this result with the fact, that one part of the polymerizable surfactant is located into the

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particle and can not help to stabilize the particles. Reb et al [9] achieved, caused by a regular distribution of carboxylic groups, a high stability with polymerizable isophthalate surfactants. The problem of stabilization with polymerizable surfactants was investigated from Asua and co-workers [10] regarding to crotonates, methacrylates and maleates. The nonreactive crotonates led to unstable emulsions. The very reactive methacrylates showed a lot of coagulum. The maleates with a medium reactivity led to stable dispersions with increased water resistance and electrolyte stability. Guyot and co-workers [11] found the same results producing styrene or butyl acrylate latexes with polymerizable maleates.

In this article, the use of commercial available surfactants is investigated. 13 nonionic types were used to produce latexes and to formulate paints.

Experimental

Latexes were produced with classical methods for emulsion polymerization. To compare the results a nonpolymerizable ethoxylated fatty alcohol has been used. Table 1 contains a typical recipe.

Table 1. Polymer recipe

Reactor charge	Water	214,1
	30% Alkyl ether sulfate	0,9
	Polymerizable surfactant	0,5
Emulsion	Water	225,3
	30% Alkyl ether sulfate	29,9
	Polymerizable surfactant	16,5
	Sodium bicarbonate	0,9
	Vinyl acetate	100,5
	Methyl methacrylate	167,6
	Butyl acrylate	212,8
	Vinyl triethoxysilane	2,5
	Methacrylic acid	1,9
	Sodium bisulfite	0,5
Initiator 1	Potassium persulfate	0,4
	Water	5
Initiator 2	Potassium persulfate	0,7
	Water	20
	Total	1000

Coagulum, viscosity, particle size and water up take were determined for all latexes. After that paints were formulated and scrub resistance and pigment stability were measured.

Table 2 contains the different polymerizable surfactants:

Table 2. Polymerizable surfactants

Name	Chem. composition	Manufacturer
Emulsogen R 109	Vinyl polyalkylene glycol ether 10 EO	Clariant
Emulsogen R 307	Vinyl polyalkylene glycol ether 30 EO	Clariant
Sinnoester CPM 1	Dodecyl polyethyleneoxid maleat 17 EO	Cognis
Sinnoester CPM 2	Dodecyl polyethyleneoxid maleat 34 EO	Cognis
Sinnoester CPM 3	Dodecyl polyethyleneoxid maleat 43 EO	Cognis
Maxemul 5010	Alkenyl/carboxyfunctional hydrophobe with 25 EO	Uniqema
Maxemul 5011	Alkenyl/carboxyfunctional hydrophobe with 34 EO	Uniqema
PEM63P	Polyalkylene glycol methacrylate	Laporte
PPM63E	Polyalkylene glycol methacrylate	Laporte
MPEG 230 MA	Methoxy polyethylene glycol 230 methacrylate	Prochema
MPEG 400 MA	Methoxy polyethylene glycol 400 methacrylate	Prochema
MPEG 550 MA	Methoxy polyethylene glycol 550 methacrylate	Laporte
MPEG 750 MA	Methoxy polyethylene glycol 750 methacrylate	Röhm

Results

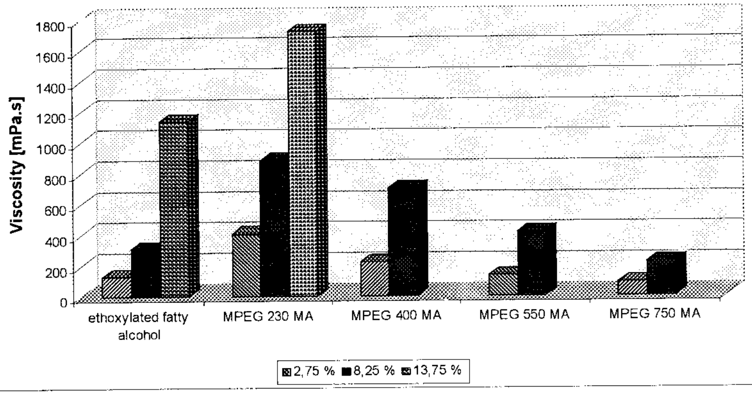
All surfactants led to stable latexes. Table 3 contains all technical datas. The solids of these latexes were about 50% and the pHs were about 5. The TG-values were measured with DSC-Spectroscopy. All values were in a range of about 11 °C.

Table 3. Technical datas of the vinyl acetate/acrylate-copolymers

	coagulum	viscosity	Water up take	Particle size	Pigment stability	Scrub resistance
	gr / 2000 gr Latex	mPa.s	%	nm		cycles
Ethoxylated fatty alcohol	0,07	128	9,3	129	No	850
Emulsogen R 109	0,1	80	12,1	176	No	550
Emulsogen R 307	0,1	64	10,9	197	No	500
Sinnoester CPM 1	0,23	420	13,1	142	No	650
Sinnoester CPM 2	2,44	65	17,7	211	No	370
Sinnoester CPM 3	4,68	64	21,2	237	Yes	500
Maxemul 5010	0,13	92	7,8	148	No	750
Maxemul 5011	0,1	136	8,3	144	No	630
MPEG 550 MA	2,44	136	16,2	147	No	370
MPEG 400 MA	0,1	224	9,5	152	No	450
MPEG 230 MA	0,1	408	7,9	136	No	430
Plex 6850-0	34,7	88	15,9	140	No	350
PEM63P	0,19	112	8,5	170	No	410
PPM63E	0,51	352	8,4	153	No	620

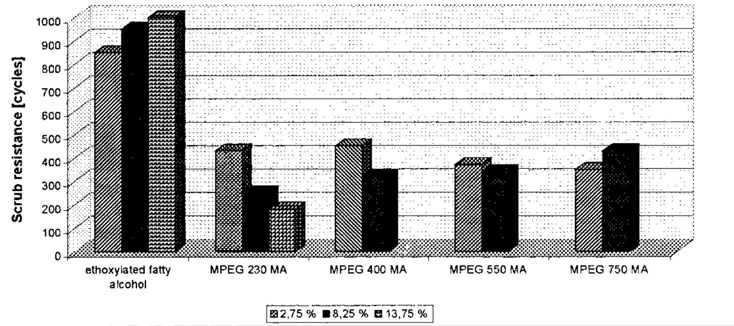
The formulated paint with the non polymerizable surfactant gave the best results. 5 polymerizable surfactants led to lower water up take and none showed a lower particle size as the non polymerizable surfactant. To explain these results tests were done with variations of the surfactant in the reactor charge. Figure 1 contains the viscosities of the latexes with methoxy polyethylene glycol methacrylate as the polymerizables surfactants.

Figure 1: Dependency of the viscosity from nonionic surfactant and reactor charge



We see a strong increase of the viscosity with increasing quantities in the reactor charge. The three methoxy polyethylene glycol methacrylates with high molecular weight led to unstable latexes at the highest reactor charge. Interesting was the decrease of the viscosity with longer chain of ethylene oxid. The viscosity correlate to the particle size. Higher viscosity led to smaller particle size. Measuring the scrub resistance we receive totally different results, seen in figure 2.

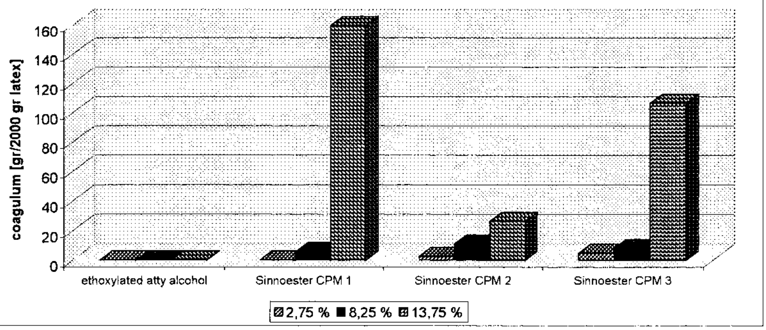
Figure 2: Dependency of the scrub resistance of a paint with 80% PVC from nonionic surfactant and reactor charge



Increasing quantities of the nonpolymerizable surfactant in the reactor charge led to higher scrub resistance. This is in contrast to what we see with the polymerizable methoxy polyethylene glycol methacrylates. A possible explanation could be that with the polymerizable surfactants one part of the surfactant is enclosed in the particle and can not take part at the stabilization of the pigments.

The Sinnoesters show another problem of polymerizable surfactants. Figure 3 contains the coagulum after polymerization.

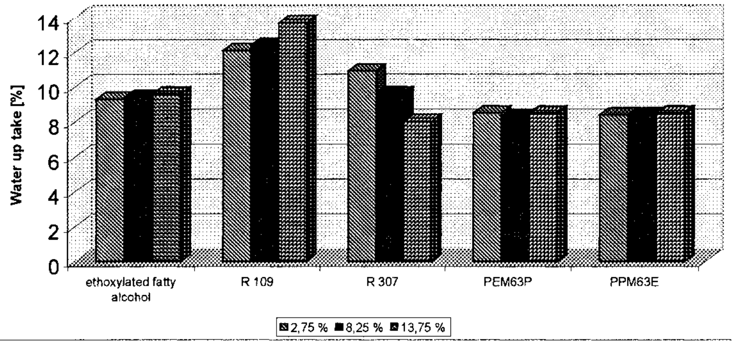
Figure 3: Dependency of coagulum from nonionic surfactant and reactor charge



Increasing the content of surfactant in the reactor charge the nonpolymerizable fatty alcohol shows that the content of coagulum remains stable. On the other hand we observe with the three Sinnoesters a strong increase of the coagulum content.

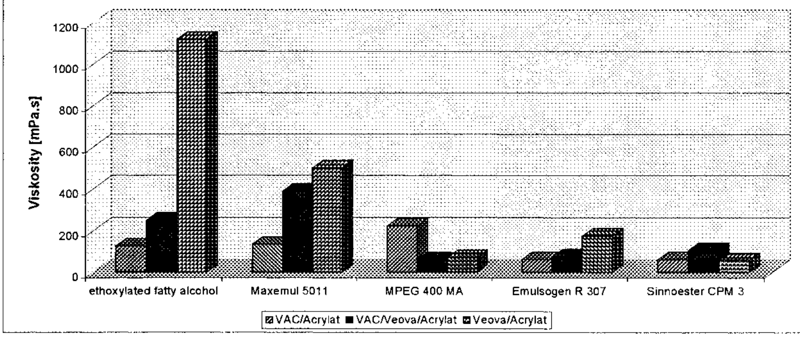
Measuring the water up take of the different polyalkyleneglycols, increasing contents in the reactor charge led to an increase or a decrease of the values, figure 4. These values correlate with the particle size. For a plausible explanation a further study is in progress.

Figure 4: Dependency of water up take from nonionic surfactant and content in the reactor charge



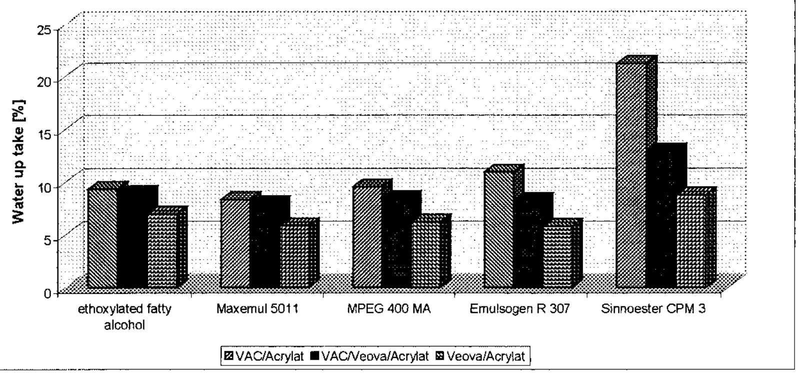
In a second step four surfactants were tested with different monomer compositions. The TG-values of these different latexes remained constant. Figure 5 contains the viscosities of these latexes. We found very different values with no correlation to particle sice or scrub resistance. The terpolymer with Emulsogen R 307 as the polymerizable surfactant showed with 1050 cycles the highest value. Generally we can say that the polymerizable surfactants show with different monomer compositions worse results than with nonpolymerizable ethoxylated fatty alcohol.

Figure 5: Dependency of the viscosity from nonionic surfactant and monomer composition



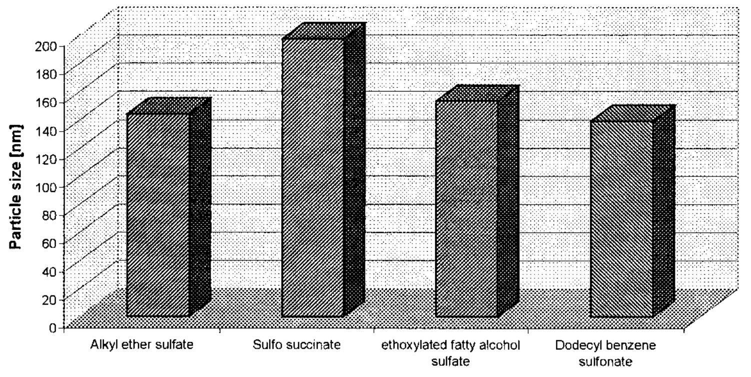
Measuring the water up take of dried films, we see a decrease of the values with increasing hydrophobicity of the monomers, figure 6. We also see smaller differences of the values. This means, increase of the hydrophobicity of the monomers lead to a smaller influence of the surfactant.

Figure 6: Dependency of the water up take from nonionic surfactant and monomer composition



In a third step we investigated the influence of the anionic surfactant. We made a combination of Maxemul 5011 with a sulfo succinate, an ethoxylated fatty alcohol sulfate and a dodecyl benzene sulfonate. Figure 7 contains the particle sizes.

Figure 7: Dependency of the particle size from anionic surfactant



The results for the particle size analysis correlate with all other measured parameters. For example figure 8 contains the scrub resistance. It seems, that the polymerizable surfactant is strongly influenced by the anionic surfactant. This result was confirmed by Asua and co-workers [12] in a mathematical model of the polymerization with polymerizable surfactants. Studies continue to increase the scrub resistance of paints, formulated with polymerizable surfactants.

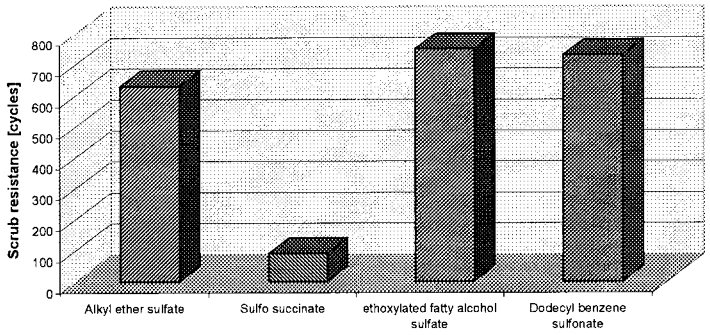


Figure 8: Dependency of the scrub resistance of a paint with 80% PVC from anionic surfactant

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