Investigation on dynamic VOC production from industrial, high solids content emulsion polymerizations

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Investigación sobre la producción dinámica de COV a partir de polimerizaciones en emulsión industriales con alto contenido de sólidos

Investigació sobre la producció dinàmica de COV a partir de polimeritzacions en emulsió industrials d'alt contingut en sòlids

ABSTRACT

Volatile Organic Compounds (VOC) pose a serious threat to human health and the environment. Unfortunately, many processes from fine chemistry involve VOCs as reagents, solvents, products or by-products. International standards and market requirements keep asking for lower VOC content in commercial goods, with the final aim of VOC-free products. Accomplishing such a task is a challenge because VOCs, due to their high vapour pressure, are hard to remove with traditional industrial methods, such as vacuum stripping or absorption. For this reason, it is important to know and understand how VOCs evolve throughout a chemical reaction. In this field, adhesives, which are usually developed exploiting polymerizations, represent an interesting subject, due to the complexity of their industrial synthesis: VOCs appear as reagents (monomers), conversion enhancers (post-polymerization), and by-products (hydrolysis and small chains). In this work, a study on the evolution and content of VOCs of an industrial recipe involving emulsion polymerizations is carried out. The industrial recipe is characterized by high solids content (about 70% w/w) and is mainly composed of 2-ethylhexyl acrylate (up to 50% w/w), anionic and nonionic surfactants. The evolution of the main VOCs found under different working conditions is discussed. The main VOCs found are acetaldehyde, acetone, t-butanol, vinyl acetate, butanol, methyl-meth-acrylate, butyl acrylate, 2-ethyl-exyl-alcohol, 2-ethyl-exyl-acetate and 2-ethyl-exyl-acrylate.

RESUMEN

Los compuestos orgánicos volátiles (COV) representan una grave amenaza para la salud humana y el medio ambiente. Desafortunadamente, muchos procesos de química fina utilizan COV como reactivos, disolventes, productos o subproductos. Los estándares internacionales y los requisitos del mercado siguen pidiendo un menor contenido de COV en los productos comerciales, con el objetivo final de obtener productos libres de COV. Lograr tal tarea es un desafío porque los COV, debido a su alta presión de vapor, son difíciles de eliminar con métodos industriales tradicionales, como la extracción al vacío o la absorción. Por este motivo, es importante conocer y comprender cómo evolucionan los COV a lo largo de una reacción química. En este campo, los adhesivos, que habitualmente se desarrollan aprovechando polimerizaciones, representan un tema interesante, debido a la complejidad de su síntesis industrial: los COV aparecen como reactivos (monómeros), potenciadores de conversión (postpolimerización) y subproductos (hidrólisis y pequeñas cadenas). En este trabajo se lleva a cabo un estudio sobre la evolución y contenido de COVs de una receta industrial que implica polimerizaciones en emulsión. La receta industrial se caracteriza por

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un alto contenido de sólidos (aproximadamente 70 % p/p) y está compuesta principalmente por acrilato de 2-etilhexilo (hasta un 50 % p/p), tensioactivos aniónicos y no iónicos. Se discute la evolución de los principales COV encontrados en diferentes condiciones de trabajo. Los principales COV encontrados son acetaldehído, acetona, t-butanol, acetato de vinilo, butanol, metacrilato de metilo, acrilato de butilo, alcohol de 2-etil-exilo, acetato de 2-etil-exilo y acrilato de 2-etil-exilo.

RESUM

Els compostos orgànics volàtils (COV) representen una greu amenaça per a la salut humana i el medi ambient. Malauradament, molts processos de la química fina impliquen COV com a reactius, dissolvents, productes o subproductes. Els estàndards internacionals i els requisits del mercat segueixen demanant un contingut més baix de COV en productes comercials, amb l'objectiu final de productes lliures de COV. Assolir aquesta tasca és un repte perquè els COV, a causa de la seva alta pressió de vapor, són difícils d'eliminar amb els mètodes industrials tradicionals, com ara l'eliminació al buit o l'absorció. Per aquest motiu, és important conèixer i entendre com evolucionen els COV al llarg d'una reacció química. En aquest camp, els adhesius, que solen desenvolupar-se aprofitant polimeritzacions, representen un tema interessant, per la complexitat de la seva síntesi industrial: els COV apareixen com a reactius (monòmers), potenciadors de conversió (post-polimerització) i subproductes (hidròlisi i petites cadenes). En aquest treball es realitza un estudi sobre l'evolució i el contingut de COV d'una recepta industrial que implica polimeritzacions en emulsió. La recepta industrial es caracteritza per un alt contingut en sòlids (al voltant del 70% p/p) i es compon principalment d'acrilat de 2-etilhexil (fins a un 50% p/p), tensioactius aniònics i no iònics. Es comenta l'evolució dels principals COV que es troben en diferents condicions de treball. Els principals COV trobats són l'acetaldehid, l'acetona, el t-butanol, l'acetat de vinil, el butanol, el metacrilat de metil, l'acrilat de butil, l'alcohol 2-etil-exil, l'acetat de 2-etil-exil i l'acrilat de 2-etil-exil.

INTRODUCTION

Volatile Organic Compounds, according to the Environment European Agency, are organic chemical compounds that under normal conditions are gaseous or can vaporise and enter the atmosphere. According to the European Directive 2004/42, they are defined as substances with an initial boiling point of 250 °C or less, measured at a standard pressure of 101.3 kPa[1]. Despite some differences in the definitions of VOC among countries [2], it is quite established that VOCs represent critical issues for human and environmental health [3].

VOCs affect many aspects of the chemical industries, involving both production and final users. VOCs are involved in the rubber industry [2], waste management [4], and polymer industry [5]. For what concerns the final users, VOC content of goods from these industries can impact final users in several ways, such as furniture [6] and paintings (in Europe, there is a specific standard for limiting the amount of volatiles in paints and coating with the EU Solvent Directive (1999/13/EC)). The polymer industry represents one of the most important frameworks affected by volatiles, involving both chemical processes and final products.

Among the different modes of polymerization, emulsion polymerization is a well-established technology to synthesize acrylate-based latexes, such as adhesives[7]. Using micelles formed with anionic and non-ionic surfactants, makes it possible to polymerize in water, avoiding the use of organic, toxic solvents [8].

However, with the constant increase by the different stakeholders involved in safer and healthier processes[9] and goods, regulations are becoming lesser and less loose on the amount of VOCs in commercial goods[10], demanding for new technologies to keep up with the more strict requirements.

The most commonly known methods to reduce volatile content in emulsion polymerization are post-polymerization, devolatilization, temperature increase and reactive comonomer [10]. However, each one comes with advantages and drawbacks. For example, post-polymerization, which is by far the most used technology in the emulsion polymer industry, can promote the development of additional VOCs, as it will also be shown in this study. Temperature increase can compromise the latex quality, and also process safety since polymerizations are highly exothermic[11]. Devolatilization may also compromise the latex quality if the temperatures required for stripping are excessively high.

In this work, a preliminary study on the evolution and content of Volatile Organic Compounds of an industrial emulsion polymerization is carried out, under different working conditions. The industrial recipe is characterized by high solids content (about 70% w/w) and is mainly composed of 2-ethylhexyl acrylate (up to 50% w/w), anionic and nonionic surfactants.

Conversion is enhanced by performing a post-polymerization phase, carried out by dosing two solutions of an organic initiator, a mixture of t-Butyl hydroperoxide and Sodium formaldehyde sulphoxylate, for 60 min. In this work, the impact of two effects on VOC development and control will be also studied: the impact of a nitrogen flowrate on reactor head, and the impact of a flash evaporation with nitrogen on the final latex. The latter is one of the most known method to reduce VOCs content in industrial latexes [5], but it is expected to find hard applications with low volatile VOCs. VOCs characterization is performed in both a traditional lab-scale recipe and with a novel method, consisting of a continuous nitrogen flow on the reactor's head after semi-batch dosing. In addition, the final latex is stripped by means of a vacuum under saturated nitrogen flow (also called devolatilization), according to a setup from the current literature. In the original

study[5], a vinyl acetate/butyl acrylate/acrylic acid latex was used, with high vinyl acetate content (78.5% w/w of total monomers). In this study, a 2-ethyl-hexyl acrylate/vinyl acetate/butyl acrylate/methyl-methacrylate latex is used (with 72% of 2-ethyl-hexyl acrylate). 2-ethyl-hexyl acrylate has a boiling point of 214°C at ambient pressure, while vinyl-acetate boils at 72°C. Hence, stripping in this work is expected to be less effective.

It is shown that, despite being one of the most common technologies in VOCs reduction for latexes, according to the working conditions imposed in this work, devolatilization is not a very effective tool to remove VOC content with high-boiling substances, while working under nitrogen stream over the course of reaction highly enhances monomer conversion.

MATERIALS AND METHODS

2.1 Lab-scale setup

All the tests were performed in a 5 L balloon, with a PTFE half-moon stirrer with a working volume of about 2L (Figure 1 a). Nitrogen flux was added by means of a rubber tube, with an inlet flow-rate adjustable with an adapter in the range of 0-60 L/h. Nitrogen comes directly from an industrial 6 bar line. For its use in lab, a pressure reducer was installed. Temperature is manually monitored, with the use of a bulb thermometer dip in the reaction environment. The jacket temperature is handled with a water bath with an electric heater.

Reagents, initiators, and post-polymerization initiators are dosed with the use of volumetric pumps. For low flowrates (below 1 mL/h, typical of initiators), a CAT DP200/20 pump with a 20V head is used, while for greater rates, a Ismatec REGLO CPF-digital pump with an RH00 head is chosen.

For what concerns the reaction environment, two different setups have been used, as shown in Figure 1: a classic emulsion polymerization (Figure 1 a), with reagents dosed by means of volumetric pumps, with a condenser for eventual vapours, and a system with a constant nitrogen flow on the reactor head, which can be vented from the same condenser (Figure 1 b). with a flowrate of about 50 L/h.

After synthesis, the final latex was stripped with the combination of nitrogen flowrate (50 L/h) and vacuum. The scheme proposed is close to a study from the literature[5], but applied to a different polymer. When applying a gas flow under vacuum, the system is quite more complicated: the system may lead to the stripping of water, compromising the latex quality. To avoid this nitrogen saturated with water was applied, as shown in Figure 3. Saturated nitrogen is made by means of two Drexel bottles installed in series on the nitrogen line and filled with water, which temperature is controlled with a thermostat. This allows for a vapour saturated nitrogen flux, that does not compromise water content in the latex. The condensed phase is recovered with a Dimroth condenser connected to the reactor head, processed with a counterflow cold water stream, and
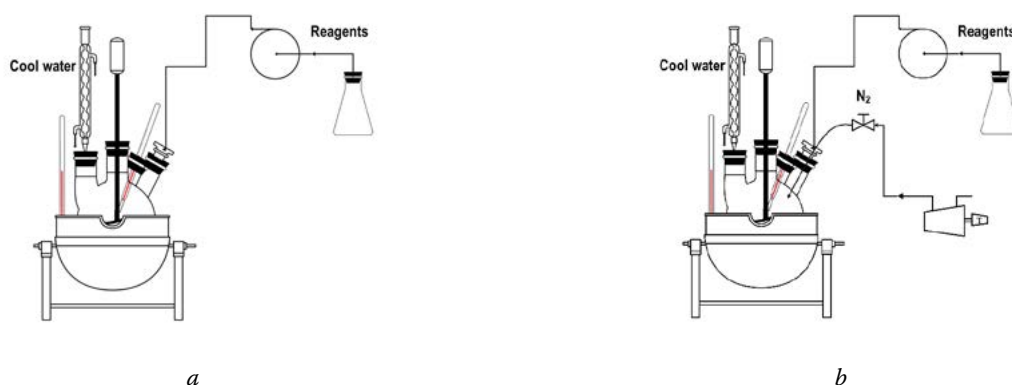

a   *b*

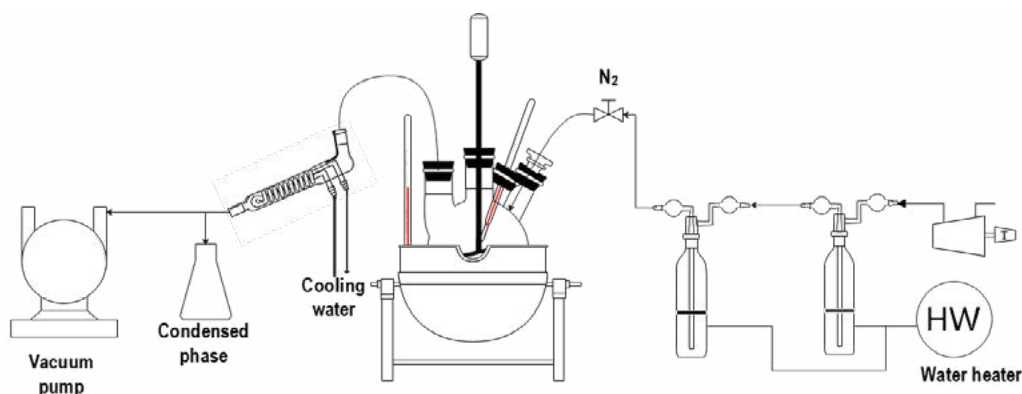**Figure 1** *Setup for latex synthesis*

Figure 3 *Setup for stripping*

tilted, so that the liquid phase can be deposited in a dedicated flask. Stripping is applied with the use of a vacuum pump. Devolatilization lasted for 2 hours, at the temperature of 60°C, with a setpoint pressure of the vacuum pump of 500 mbar. The water inside Drexel was kept at the temperature of 70°C, to heat the inlet cool nitrogen up to working conditions. Such conditions are moderate for a stripping, but it is required to preserver latex quality, in a vision of a possible industrial scale-up.

Also, foam could be generated with this type of additions [5]. No foam control device was installed, but foaming was never experienced over every test performed.

2.2 Analytical method

Every sample was analysed through a Gas Chromatography – Flame Ionization Detector (Agilent 7890A, Agilent Technologies, Milan, Italy). The method foresees a split injection 1:30 with the injector temperature set at 200°C. The temperature ramp for the analysis is set from 45°C to 250°C. Samples are separated inside an Agilent DB-624 Ultra Inert column.

Every substance detected is determined quantitively according to specific standards.

2.3 Recipe and tests performed

Emulsion polymerizations were performed with a synthesis of a high solids content latex, at about 65.26% w/w, mainly composed of 2- ethyl-hexyl acrylate. The composition is the following: demineralized water (34.74% w/w), water-phase initiators (0.30%), anionic and nonionic surfactants (1.11% w/w), 2-ethyl-hexyl acrylate (45.56% w/w), butyl acrylate (8.65 % w/w), vinyl-acetate (4.55 % w/w), methyl-methacrylate (4.55% w/w), and the total amount of organic initiators is 0.54% w/w (mainly t-butyl-hydroperoxide,TBHP). The synthesis is performed according to this scheme: loading of a mixture of water and surfactants, heating up to 80-81°C, loading of water-phase initiator, semi-batch phase while keeping the temperature at 81°C, with continuous dosing of a pre-emulsion and water-phase initiators for 4.5 h, post-reaction (60 minutes), and a final post-polymerization (60 mins).

At first, regular emulsion polymerization has been carried out, within a closed environment, where only reagents are added, and eventual vapours are sent-back in the reactor with the use of a condenser. A single test was performed, named A. Secondly, the impact of a continuous nitrogen flow on the reactor head was studied (tests B1 and B2). In this case, a nitrogen flow-rate equal to 50 L/h was applied after the semi-batch dosing and applied up to the reaction end. A summary of the experiments is reported in Table 1. After the end of each experiment, stripping with saturated nitrogen and vacuum was applied, and the condensed phase was also analysed.

Table 1 *Summary of tests performed*

Test	A	B
# of tests	1	2
Nitrogen flux	No	Yes

Samples were collected at the following times: half of the dosing during the semi-batch phase, end of dosing, after the post-reaction, and the final product (see Table 2). Considering the potentially high amount of residual monomer, samples require quenching, performed by adding an aqueous solution saturated with 4-methoxy phenol to the sample (0.24% w/w). Samples are then sent for analysis. The reliability of the samples is additionally verified through the determination of the alcohol/acetate ratio.

Table 2 *Summary of samples analysed*

	Sample ID	Time elapsed:
Half dosing	HD	165 min
End of dosing	ED	300 min
Post-reaction	PR	360 min
Final	F	420 min
Condensed phase	C	540 min

RESULTS AND DISCUSSION

Table 3 reports all the identified VOCs over the course of the reaction, without including the stripped latex. From GC-FID analyses, the most notable substances found are: acetaldehyde, acetone, t-butanol, vinyl acetate, butanol, methyl-methacrylate, butyl acrylate, 2-ethyl-exyl-alcohol, 2-ethyl-exyl-acetate and 2-ethyl-exyl-acrylate.

2-ethyl-hexyl-acetate is also measured because, as it is present inside 2-ethyl-hexyl-acrylate is also measure with a known composition and it is stable during the reaction, it is used as an index to estimate the reliability of the sample. It can be noticed that, in sample B2, the acetate content is slightly higher than the A and B1. This is because a different batch of 2-ethyl-exyl-acrylate, even if from the same provider, was used. Indeed, alcohol/acetate ratios are similar for A and B1, and different in B2. However, the values are similar among samples of the same test, showing the reliability of the measures performed.

Monomer accumulation is always critical, with high ppm of unreacted monomers both at half dosing and at the end of the dosing. For what concerns the comparison between standard and nitrogen flux conditions, the presence of nitrogen flow greatly helps in reducing the total VOCs content, leading to a reduction of about 50% in both tests B1 and B2. It should be noted that nitrogen flow starts after the semi-batch period, so samples until this time mark are quite similar, as expected.

Tert-butanol (Figure 5) and acetone are found only in the final product, highlighting the impact of post-polymerization. Tert-butanol is reasonably derived from the rupture of the peroxidic bond of TBHP. As highlighted in this literature work[12], β-scission of the tert-alkoxyl radical yields acetone, and hydrogen abstraction gives t-butanol. Those species are not developed over the course of the regular polymerization.

According to the amount dosed, between 20% and 40% of peroxide is converted into tert-butanol. Butanol is found in almost constant amounts over the course of each test. Acetaldehyde (Figure 6) seems controlled

Table 3 *Trends of VOC over the experiments (HF: half dosing, ED: end of dosing, PR; post reaction, F: Final)*

9	HD	ED	PR	F	HD	ED	PR	F	HD	ED	PR	F
Test	Acetaldehyde				Acetone				T-butanol			
A	335	0	455	599	0	0	0	392	0	0	0	661
B1	384	411	156	0	0	0	0	167	0	0	0	392
B2	431	0	278	0	0	0	0	169	0	0	0	394
Test	Vinyl acetate				Butanol				Methyl-methacrylate			
A	14561	11101	7616	2714	72	32	69	78	1281	762	13	40
B1	15295	11263	3164	463	74	58	69	69	1289	895	15	33
B2	11474	10481	3119	342	89	75	86	80	865	408	7	33
Test	Butyl acrylate				2-ethyl-hexyl-alcohol				2-ethyl-hexyl-acetate			
A	6460	3339	123	6	485	418	592	574	304	317	314	333
B1	6194	3761	196	7	451	432	541	581	300	323	332	325
B2	4469	2780	111	13	448	481	504	563	524	651	591	585
Test	2-Ethyl-exyl-acrylate				Tot VOC				Alcohol/acetate			
A	36458	17604	794	45	62656	35684	12094	6479	1.59	1.32	1.88	1.72
B1	33083	19906	1390	47	59060	38967	7990	3231	1.50	1.34	1.63	1.79
B2	23028	15424	811	48	42364	31771	7468	3651	0.85	0.74	0.85	0.96

by nitrogen, with lower amounts of acetaldehyde after one hour, and no acetaldehyde found at the end of tests B1 and B2.
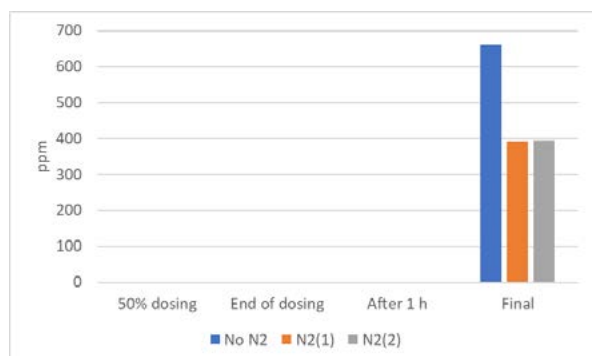

Figure 3 *Tert-butanol content in the tests performed*
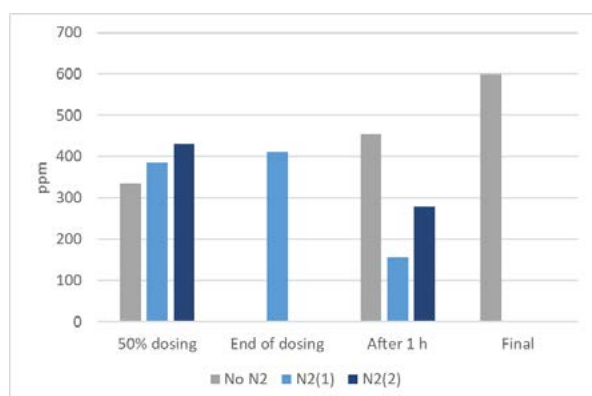

Figure 4 *Acetaldehyde content in the tests performed*

Vinyl acetate is the only monomer remarkably affected by nitrogen, showing a greatly enhanced conversion (Figure 7). Butyl-acrylate, 2-ethyl-exyl-acrylate and methyl-methacrylate are not particularly sensitive to nitrogen flux.
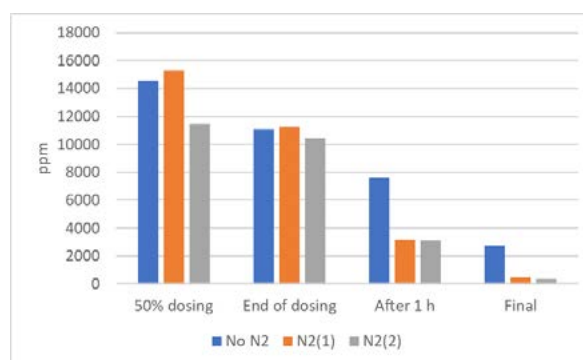

Figure 5 *Vinyl acetate content in the tests performed*

Test B2 shows higher conversion for all the monomers dosed along the semi-batch phase compared to the other tests. This may be related to a better reaction startup: emulsion polymerizations are well-known to exhibit low reproducibility. In this case, the pre-emulsion is dosed on a very small amount of water loaded with surfactants. The level is so low that detecting the exact temperature of the water is hard. This is a crucial aspect to grant a proper radical initiation of the polymerization, and it is hypothesised that in test B2, a better polymerization initiation occurred. However, VOC concentration at the end of the test is quite similar.

From the results, it is shown that, while post-polymerization increases conversion even beyond 99%, it leads to the development of undesired VOCs, such as t-butanol and acetone. 2-ethyl-hexyl-alcohol is also a crucial component, apparently unaffected by nitrogen flow. Its values are quite similar along every test, but it appears to slowly increase overtime. The hydrolysis of 2-ethyl-hexyl-acrylate would lead to 2-ethyl-hexyl-alcohol and acrylic acid. Acrylates are well-known to be subjected to hydrolysis, according to different mechanisms [13,14], but it is very complex to find out if

monomer hydrolysis is a relevant phenomenon in such a complex system.

For what concerns the reason behind the effect of nitrogen on VOCs content, one of the possible reasons behind this can be related to the removal of oxygen from the reaction environment. Monomers, due to their innate reactivity, are usually stabilized with the addition of inhibitors such as hydroquinone or methoxyphenol [15]. 2-ethyl-hexyl-acrylate, the most abundant monomer used in the recipes, uses hydroquinone monomethyl ether (known as MeHQ) as inhibitor at 30 ppm concentration, according to the Safety Data Sheet. Inhibitors can be removed from monomers, using distillation or co-precipitation methods. However, this is a solution applied most in laboratory studies. In real industrial cases, working with great volumes, it is too unsafe to remove the inhibitors from the monomer solution, and syntheses are usually carried out without removing the stabilizers. Usually, these inhibitors use oxygen to promote radical reactions that act as a generator of radical scavengers, which block monomer homopolymerization [15]. Oxygen is usually naturally dissolved in the liquid phase.

In this study, monomers have not been treated, so both inhibitors and dissolved oxygen are available in the reaction environment. In conclusion, our hypothesis on the role of nitrogen is the removal of oxygen, deactivating the effect of monomer inhibitors.

For what concerns the application of the stripping, significant results were found for vinyl-acetate applied for case A, where the content is high (about 2700 ppm). No remarkable results have been identified for the other species. This is due to the mild conditions of stripping. Indeed, vinyl acetate was the only specie identified in the final condensate sample of test A, associated with a reduction of vinyl acetate (up to 300 ppm). For the other VOCs, no significant reduction was observed.

CONCLUSIONS

In this work, a study on VOCs development over the course of an emulsion polymerization of a high solids content latex was studied. The generation of VOCs was studied both with a regular synthesis and under nitrogen flow. From the results, a wide set of VOCs have been identified. Some are simply unreacted monomers, some are due to the post-polymerization initiators, such as tert-butanol from TBHP, and other are likely developed over the course of reaction, due to side-reactions and short polymer chains. In general, working under nitrogen flow favours the reduction of the total amount of VOCs (down to about 50% if compared to the standard recipe), showing the best results for t-butanol and acetaldehyde final content. This means that, the presence of nitrogen enhances the process chemistry, increasing monomers conversion and selectivity towards desired products. Our take on this consists in the removal of oxygen residues, which is a well-known activator of monomer inhibitors. By removing oxygen from the environment, monomers reactivity is naturally promoted. Moreover, devolatilization was effective only

for vinyl-acetate with very high concentrations (above 2700 ppm in the final latex), hence stronger conditions may be required (such as higher temperatures), but this may threat the final latex quality.

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