New emulsifiable MDI-variants for sealers and primers on dry and wet concrete

Marc Broekaert

Application and Product Development Manager - Coatings
Huntsman Polyurethanes
Everslaan 45
B3078 Everberg, Belgium
Tel. +32 2 758 8814
marc_broekaert@huntsman.com

Abstract

The use of water-reducible coatings is important due to environmental factors. However, in the case of isocyanate-reactive coatings, water presents a problem, as it reacts with the isocyanate groups. Responding to different local requirements on VOC-levels, Huntsman has developed a new generation of emulsifiable diphenylmethane diisocyanate (MDI).

The products fall into two categories: high NCO emulsifiable isocyanates, which can be used for sealers on concrete, as cross-linkers with castor oil or in water-borne dispersions; and emulsifiable pre-polymers, which are useful for film-forming, water-reducible, one component coatings.

This paper details the handling, the application and the performance of emulsifiable MDI on porous substrates like concrete.

Introduction

The Directive 1999/13/EC on the limitation of emissions of volatile organic compounds (VOC) addresses the use of organic solvents in coatings. Organic solvents are used to facilitate the application of adhesives, coatings and inks, after which they evaporate. They are also used to clean the surface prior to the coating activity and to clean manufacturing and application equipment.

The implementation of the Directive 1999/13/EC forces the majority of companies active in the manufacturing and application of coatings to monitor and control their VOC emissions over the coming years.

Raw material manufacturers have responded to the need for lower VOC emissions with the development of high solids to 100% solids coatings, UV curing and powder coatings, and last but not least, the water-reducible and water-borne coating technology.

Isocyanates react with water, causing significant technical problems, which need to be overcome. Due to these problems, the first waterborne isocyanate coatings were based upon non-reactive urethane dispersions. Isocyanate crosslinkers for water-borne coatings have also been on the market for several years.

The aromatic MDI and MDI-variants are used in protective coating systems for multiple industrial and construction applications. Hydrophobic species like MDI can be modified by introducing hydrophilic solubilising groups to become easily emulsifiable in water, but MDI is also very reactive, with water. This paper will discuss the advantages and disadvantages of emulsifiable MDI-variants and their applicability on a porous substrate such as concrete.

Products and applications

To make the isocyanate emulsifiable, it is modified with specific isocyanate-reactive surfactants with a hydrophilic character. Huntsman owns several patents covering this technology.

During the preparation, application, drying and curing process, the following chemical reactions occur :

1. Reaction of free isocyanate-groups with hydroxyl groups on the methoxypolyethylene glycol, building the hydrophilic group on the isocyanate
2. Reaction of free isocyanate-groups with free hydroxyl groups on the castor oil or on the polyol in the emulsion
3. Reaction of free isocyanate-groups with water present in the blend at the moment of application
4. Reaction of free isocyanate-groups with humidity present in the substrate or in the environment after evaporation of all volatile components present in the blend

The products used for this study are different in functionality and in free NCO-content.

Table 1*: Properties of the emulsifiable MDI-variants*

	% NCO (± 0,5%)	Viscosity, Typical value @ 25°C, mPa.s	Average Functionality
Suprasec 1042	29,9	275	2,7
Suprasec 2405	28,4	150	2,1
Suprasec 2408	15,3	3500	2,4
Suprasec 2419	14,4	1200	2,1

Depending on their composition, emulsifiable isocyanates can be used in the following ways:

1) As a basis for emulsifiable prepolymers with good film forming properties and tailored film properties;
2) Diluted with water, as a sealer for porous substrates like concrete and wood;
3) As a cross-linker for polyol-emulsion based two component waterborne coatings;
4) Or as a resin for water-reducible, one component polyurethane primers.

Properties

Storage stability

To be able to determine the shelf life of the modified MDI variants, the products were stored at 40°C and at 50°C. The pressure build-up, the NCO-values and the viscosity at 25°C were all measured.

***Table 2** : Storage stability of EID 9304* produced and stored at 50ºC or 40ºC*

Storage temperature	50ºC		40ºC	
	% NCO	Viscosity (cps,25ºC)	%NCO	Viscosity (cps,25ºC)
1 day	27.86	57.0	27.83	57.0
2 days	28.02	57.0		
3 days	27.85	58.0		
4 days			27.18	59.0
5 days			28.13	59.0
6 days	27.87	58.0	27.95	59.0
1 week	27.79	58.0	27.71	60.0
2 weeks	27.41	66.0	27.56	72.0
3 weeks	27.19	71.0	27.54	70.0
4 weeks	27.78	71.0	27.88	73.0
5 weeks	27.93	72.0	27.86	74.0

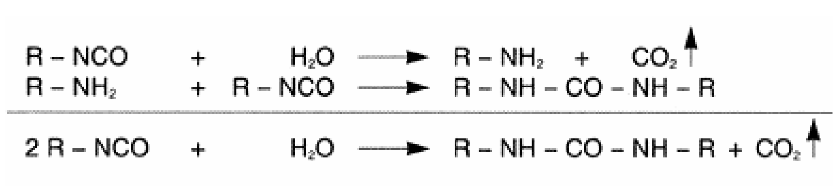
* EID 9304 is the first version of Suprasec 2405

The measured values over five weeks for the NCO and the viscosity at 25°C for the experimental product EID 9304, stored at 40°C and at 50°C, show clearly that the product stays stable for longer periods.

During five weeks of storage at the elevated temperatures, no signs of pressure build up such as bulging tins or hissing noises when opening the tins were detected.

Stability of the mixture with water

The CO_2-formation can be used to explain the chemical stability of the blend. The reaction of isocyanates with water proceeds in two steps and consumes two isocyanate groups to produce one CO_2 molecule.



(slow)

(fast)

At low mole fractions of CO_2 in water, Henry's law can be assumed to apply:

$$p_{CO_2} = k\, m_{CO_2}$$

With p_{CO2} the molar pressure of the CO_2 vapour, m_{CO2} the molality of CO_2, and k a constant for a given temperature. In this case k = 29.3 atm mol^{-1} kg H_2O. As the volume is fixed in the bottle, the partial molar pressure will increase, as the reaction proceeds and the amount of CO_2 dissolved in the water will also increase. This will also shift the acid/base equilibriums.

Figure 1 shows the experimental set-up used. A total volume of 50 ml of a 10% emulsion of the isocyanate is placed in a pressure bottle. The cap is closed using a special cap press. The bottle is placed onto a magnetic stirrer and connected to a manometer reading a differential pressure.

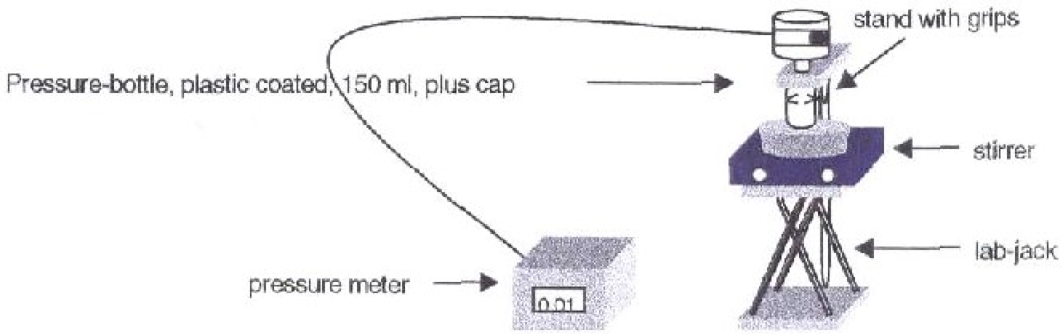


***Figure 1**: The experimental set-up used for the manometer experiments*

Figure 2 depicts the loss of NCO groups of an aqueous emulsion of Suprasec 1042 and Suprasec 2405 as a function of time. As illustrated, the consumption of NCO groups is rather slow, after four hours, when the sample is already flocculated, roughly 85% of the initial NCO groups of Suprasec 1042 and more than 90% of the initial NCO groups of Suprasec 2405 is still present.

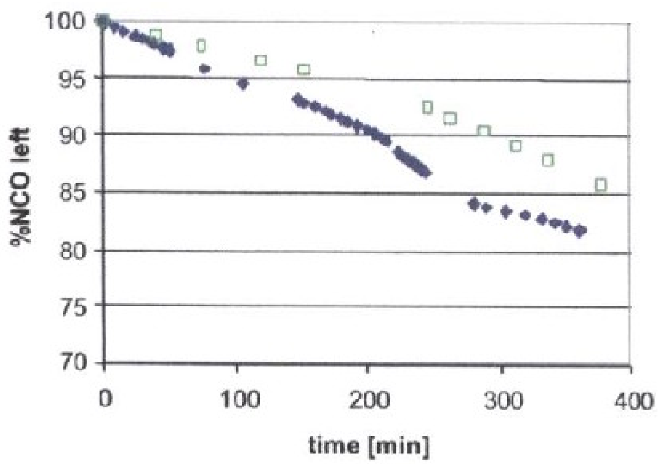


***Figure 2**: Loss of NCO with time for a 10% aqueous emulsion of Suprasec 1042 (♦) & Suprasec 2405 (□)*

Although the consumption of NCO groups is rather slow, the pot life of the blends can be quite limited because of the foaming and the phase separation.

For Suprasec 2408, the effectiveness of the primer as a function of the time between the preparation of the mixture with water and the application to the substrate was made to determine the pot life or effective working time for a blend of isocyanate and water. Suprasec 2408 was mixed in a ratio 40/60 with water, the optimum mixing ratio according to the optimisation testing. The mixture was then applied on humid concrete immediately after the mixing and then every half an hour for five hours. An additional application was made after 24 hours. The adhesion was tested under ISO4624 pull off adhesion test conditions. Although the surface quality visibly changes when the mixture is older than one hour, all samples applied within the first five hours showed a cohesive failure in the concrete at 4-5 Mpa. The sample applied after 24 hours achieved only half of the adhesive force.

Optimal mixing ratio with water

To determine the best possible mixing ratio of eMDI/water for the different emulsifiable isocyanates, the film forming capability, applicability and the concrete surface improvement were evaluated through an adhesion test.

The adhesion test was evaluated on pull off value and the nature of the failure. The adhesion test results for the different mixing ratios with water are shown in Figure 3. For the high NCO products, Suprasec 1042 and Suprasec 2405, the best results are obtained for the mixtures containing a high amount of water. For the emulsifiable pre-polymers Suprasec 2408 and Suprasec 2419 the best adhesion results were obtained for the high isocyanate-concentrated mixtures.

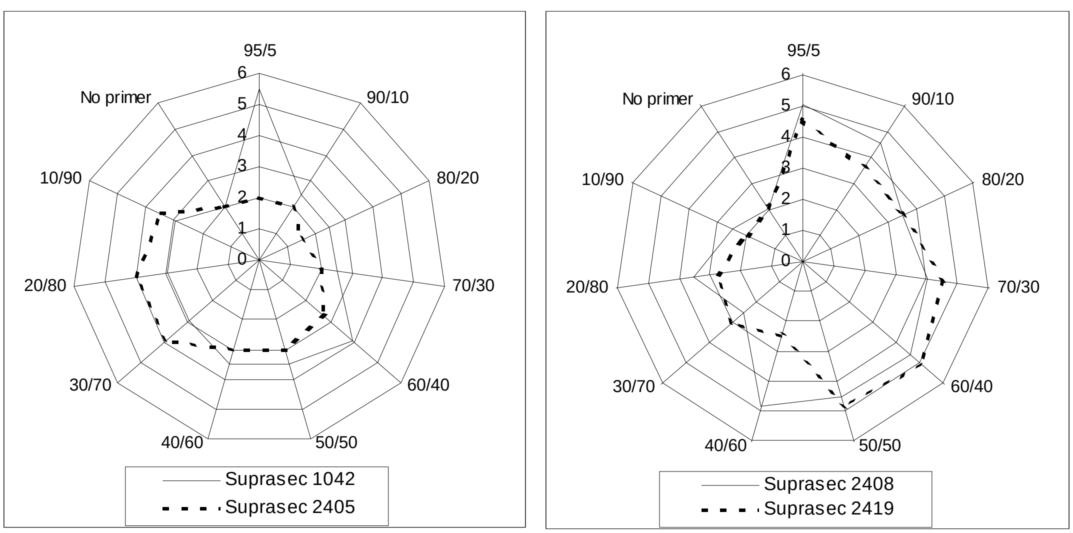


Figure 3*: Pull-off adhesion for the emulsifiable isocyanates as a function of the dilution factor, compared to a non-treated concrete surface.*

The nature of the adhesive failure for the high NCO-products Suprasec 1042 and Suprasec 2405 is cohesive in the concrete and again for the blends made with a higher amount of water. The higher amount of water results in low viscosity with good penetration in the substrate and therefore a better consolidation of that substrate. The pre-polymers Suprasec 2408 and Suprasec 2419 give cohesive failure in the concrete for all mixing ratios.

Table 3*: Adhesion failure as a function of the dilution factor*

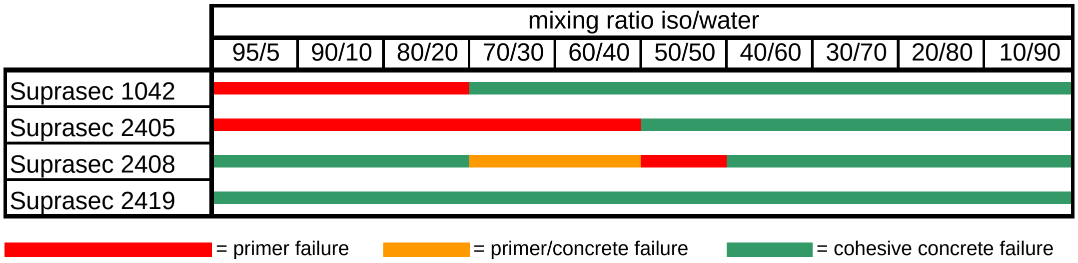


Table 4 *: Film forming on glass as a function of the dilution factor*

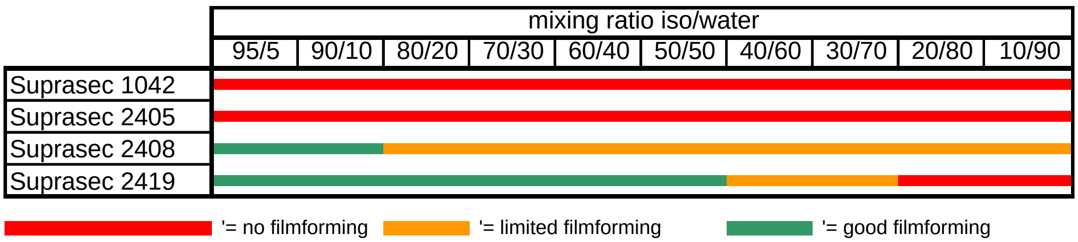
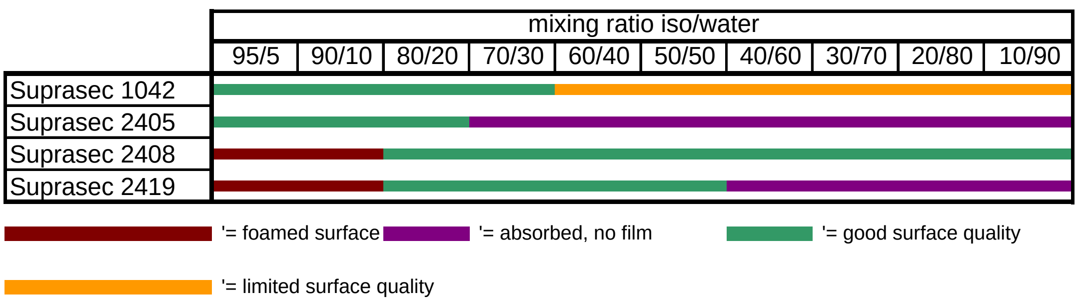


Table 5*: Film on concrete as a function of the dilution factor*



The film forming performance was tested by applying thin films on glass. As expected, the high NCO-containing isocyanates Suprasec 1042 and Suprasec 2405 did not form a film at all. The pre-polymers Suprasec 2408 and Suprasec 2419 performed best for the mixtures with higher isocyanate concentrations. Because of the absorbing property of a porous substrate like concrete, it was also interesting to see how the products behave on concrete, especially the pre-polymers with film forming capacity. With only small amounts of water used, penetration of the concrete is limited with some foaming occurring in the applied film. Once the products are diluted with 20% of water or more, the film quality improves significantly. Because of the lower starting viscosity, Suprasec 2419 only provides a limited surface quality for the higher water dilution mixtures because of the penetration in the porous substrate.

Table 6 provides an overview of the best performing water/isocyanate blends made and which will be evaluated on their pot life stability. The blend ratios were chosen based on a combination of the results of the adhesion force, the nature of the adhesive rupture and the film quality on glass and concrete. The products were blended and checked on foaming and phase separation over time. Figures 4 and 5 demonstrate the evolution of the blends as a function of time.

Blends 1 and 2 are low viscous because of the low starting viscosity of the high NCO isocyanates Suprasec 1042 and Suprasec 2405. The low viscosity results in a fast phase separation after mixing. Earlier work showed that only a limited amount of the NCO groups react in the first 24 hours. The mixtures are still applicable but will need to be stirred before use or be constantly stirred between the moment of mixing and the application. The lowest viscosity blend 2 separates the fastest, in about two minutes.

Table 6*: Start of phase separation in the optimal isocyanate/water blends for the emulsifiable isocyanates tested*

	1	2	3	4	5
Isocyanate	Suprasec 1042	Suprasec 2405	Suprasec 2408	Suprasec 2408	Suprasec 2419
Mixing ratio with water	60/40	30/70	95/5	40/60	70/30
pH blend*	3,05	4,00	3,10	3,80	3,90
Phase separation	6 min	2 min	8 min	30 min	5 min

* pH of demineralised water = 6,20

Figure 4 *shows the blends 1 to 5 after 4 and 6 minutes*

Figure 5 *shows the blends 1, 2 and 4 after 10, 30 and 90 minutes*

Although blends 3 and 4 were made with the same Suprasec 2408, the test shows that the stability of the blend depends on the mix ratio isocyanate/water. Due to the small amount of water in blend 3 (mixture 95/5), the dilution is limited and the carbon dioxide produced makes the system foam rapidly.

Blend 5, made with Suprasec 2419 in a 70/30 mixing ratio with water, is very reactive and because of the high amount of isocyanate in the blend, starts to foam almost immediately.

Film performance.

Comparative testing against solvent based, comparable systems resulted in similar performance results. Adhesion tests on dry and humid concrete also gave comparable test results for systems based on emulsifiable isocyanates against one or two component polyurethane systems that are known to perform well in such cases. Table 7 indicates that for normal cure speed polyurethane systems, the adhesion values are of the same order of magnitude as we would expect without a base coat. However, for faster cure systems like polyurea, where substrate wetting by the topcoat is not evident, there is clearly an advantage to using a primer or sealer. Certainly in the case of polyurea, that itself is not sensitive to humidity during the curing process, the systems based on emulsifiable isocyanates have a better overall performance than the traditional solvent-based polyurethane systems.

***Table 7**: Adhesion of a total system as a function of time between layers*

Topcoat / Basecoat		1 K Polyurethane ACE1014-I3			2K Polyurethane ACE0759-B7			2K Polyurea ACE1041-S2		
		Time between layers (days)								
	Based on	0,5	5	8	0,5	5	8	0,5	5	8
Sealer	Suprasec 1042	5,3	5,0	5,1	2,5	4,8	5,2	2,0	2,0	2,3
	Suprasec 2405	4,6	5,0	5,5	2,3	4,5	5,3	3,0	3,0	2,5
1K primer	Suprasec 2408	4,9	4,5	3,6	4,6	4,0	3,5	3,8	4,8	4,4
	Suprasec 2419	4,7	4,6	3,0	2,5	2,2	3,5	2,0	3,8	3,5
2K primer	Suprasec 1042 + castor oil	5,4	4,5	5,0	4,5	5,0	4,6	1,5	3,0	4,0
	Suprasec 2405 + castor oil	5,0	4,8	4,5	3,4	4,8	4,4	3,5	4,5	4,6
No basecoat		4,5			4,4			2		

Conclusions

Environmental pressures are forcing the coatings market to switch to low VOC technologies. Waterborne systems in general and emulsifiable isocyanates in particular offer alternatives to the coatings industry to comply with the changing regulations.

The first goal is to supply products that deliver similar features and performances to existing commercial technologies. The range of emulsifiable isocyanates now available can be used to make water-reducible sealers and primers, and crosslinkers for waterborne coatings.

The limiting factor for the use of emulsifiable MDI variants is the high reactivity with water resulting in stability problems for the blends and short working times. The emulsifiability of this range of products makes them very suitable for porous substrates like concrete, certainly in varying and/or high humidity conditions. The biggest advantage is obtained when fast curing systems need to be applied in difficult conditions.

As it is a fairly new and different technology, an adapted approach in manufacturing, handling and applying is needed to ensure the use of emulsifiable isocyanates in coating applications is a success.

Since we are still dealing with reactive chemicals correct protective clothing should be worn during the manufacturing, packaging and application of emulsifiable isocyanates.

Acknowledgement

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