



# BRINGING OUTSIDE COATINGS INSIDE LIMITS

ADH-free water-based binder for durable, EU Ecolabel-compliant lasure coatings. By Massimo Longoni, EPS B.V., Netherlands.

**Formulators have relied on cross-linkers such as adipic acid dihydrazide (ADH) as a way of enhancing the performance of exterior wood coatings despite this being a hazardous substance. A new polymer has now been developed that retains the durability of the final coating and offers an environmentally friendly solution to comply with the EU Ecolabel.**

In the past two decades the environmental impact of products has become a key discussion point in the European Union and a development focus for paints and varnishes producers. One of the main outcomes of the EU effort in this area was a voluntary programme to recognise environmentally friendly products. The EU Ecolabel award [1] aimed to promote products that present a reduced environmental impact throughout their life cycle and, no less important, to provide customers with environmental impact information based on scientific data. As of September 2015, 10% of all labels awarded had been given to products in the paint and varnish sectors [2, 3]. The ecological criteria of the EU Ecolabel award are product or service specific and are not everlasting. In fact, the requirements are updated regularly to take account of innovations and regulatory changes that affect the specific field of interest. In 2016 the paints and varnishes evaluation criteria were reviewed in terms of the hazardous content in the final material and a new category covering indoor and outdoor products was introduced [4]. Depending on the type of paint or varnish, some or all of the performance criteria are taken into consideration.

Requirements for solvent and hazardous material content are fixed and mandatory for all types of paint and varnish but derogations to the

use/presence of certain substances in final products are allowed when 'hazardous' substances are necessary to maximise durability in real-life conditions. Consequently, substances that are hazardous to the aquatic environment and normally banned in the EC may be permitted.

The Ecolabel classification method was introduced to help consumers identify products with lower environmental impact, which is why it is of particular interest in consumer-focused coatings sectors: interior paints, exterior paints, wood lasures, etc.

The term lasures identifies DIY low-solid varnishes for exterior wood. The main task of these kinds of products is to protect and decorate exterior wood, extending the life of wood and wooden products without gloss loss and minimal/no structural damage.

## LOW LEVELS OF ADH PERMITTED

Acrylic dispersions (AC) represent the best class of water-based polymers for exterior applications. When compared with other polymer technologies, AC offer a better balance between cost-performance and environmental benefits. But not all offer good outdoor durability; the combination of monomer composition and cross-link density are key determinants in achieving high performance. Various monomers and compositions can be used for good performance initially, but using a low-temperature cross-linker, primarily adipic acid dihydrazide (ADH), is mandatory to enhance the final performance of those so-called self-cross-linking acrylics.

In the literature, introducing ADH as a room temperature cross-linker is reported to have major benefits for block resistance, water resistance

## RESULTS AT A GLANCE

- Conventional ADH-based polymers used in the architectural exterior wood segment are hazardous to the aquatic environment.
- The aim of this study was to develop a new acrylic polymer without ADH and offering equal or better performance than those currently available.
- Optimising the polymer backbone and cross-linker achieved these goals.
- Two new products provide an EU Ecolabel-compliant solution for exterior wood coatings that retain high durability of the finished coating.

and outdoor durability; all aspects necessary for good exterior lifespan. The mechanism of the ADH cross-linking reaction is a Michael's Addition [5,6], which occurs at low curing temperature between hydrazide groups and available CO double bonds, resulting in new cross-links between the acrylic polymer chains in the dried film. At the beginning of 2016, ADH producers requested that the ECHA reclassify the product as hazardous to the aquatic environment (Chronic Category 2) with the associated hazard statement H411. In theory this new classification means that ADH does not meet Ecolabel criteria. This would have meant the EU Ecolabel award being withdrawn from all the products containing ADH. The Commission Decision (EU) 2016/397 [3] granted a derogation for the presence of 1.0% ADH max in finished paints and varnishes, stating that there are no alternative technologies that enable the same durability to outdoor products. The derogation was required to achieve the longer lifespan of finished goods combined with the overall lower environmental impact.

A key research area of the EPS technical center, the Netherlands, in the last couple of years has been a specific focus on developing ADH-free acrylics to find an alternative solution.

## NOVEL POLYMER DEVELOPMENT

The EPS research and development center has worked intensively to optimise a new acrylic polymer without using ADH or acetoacetoxyethyl methacrylate (AAEM) – sometimes associated with yellowing – suitable for architectural exterior wood applications. The main aim was to determine a new acrylic polymer to produce an EU Ecolabel-compliant coating with no environmentally hazardous components.

Table 1: Acrylic polymer specifications.

	Solids [%]	pH	MFFT [°C]	Particle size [nm/mean]	Cross-linker
Comm ADH	44	7.0-8.0	<5	55	√ (ADH)
Std ADH	44	7.0-8.0	<5	55	√ (ADH)
Std ADH-free	44	7.0-8.0	<5	60	×
ML-745	44.5	7.0-8.0	<3	50	√
ML-745-A	44	7.0-8.0	0	55	√
ML-747	44.5	7.0-8.0	<3	50	√

Primarily, different two phase-polymers with various monomer compositions and alternative cross-linkers were investigated to identify the optimal ratio that could guarantee a minimum film forming temperature (MFFT) of zero, or close to zero, and good performance.

A new polymer was considered a valid option if it achieved block resistance, water and early water resistance, and could produce a solvent-free formulation. Having zero VOC would be a plus if the new polymer was comparable to the standard technology and was in line with the core message of the EU Ecolabel. Table 1 shows a selected number of the synthesised polymers, limited in order to show the most interesting ones compared to internal standards.

The 'Comm ADH' sample is an acrylic polymer widely used in the architectural exterior wood segment. Samples 'Std ADH' and 'Std ADH-free' are EPS internal references: the first is a proven, commercially available product that contains ADH, the second is the same product but without ADH. These two are listed to show how ADH impacts performance in terms of the fixed polymer backbone and morphology. ML-745 and ML-745-A are characterised by the same cross-linking mechanism but the monomer composition presents minimal differences so that the second phase of ML-745 is harder than ML-745-A. ML-747 is an improved version of ML-745-A presenting the same monomer composition and two-phase combination but with the introduction of a different cross-linker.

The results of the broad study show that it is possible to achieve the target milestones with just the correct combination of cross-linker and polymer backbone.

The block and water resistance of the listed polymers relates to the non-formulated polymer – directly applied, 100 micron WFT (wet film thickness), on black Leneta foil and dried under standard conditions (50% relative humidity and 23 °C) prior to testing.

Block resistance is measured by applying a 0.5 kg x cm<sup>2</sup> weight pressure in one set of samples at room temperature for 24 hours (Figure 1), and 0.5 kg x cm<sup>2</sup> weight pressure to a second set of samples for 1 hour at 50 °C (Figure 2). Test results are rated on a scale of 1-5 where 5 is the best and 1 a complete failure.

Water resistance (Figure 3) is tested again on polymer films applied on black Leneta after 24 hours drying time in standard conditions and

Table 2: Acrylic polymer specifications.

	ML-19-E	ML-39-D
ML-745	50	
ML-747		50
Defoamer	0.40	0.40
Deaerator	0.50	0.50
Substrate wetting agent	0.20	0.20
Neutralising agent	0.10	0.10
"Texanol"	1.00	1.00
UV absorber	1.00	1.00
Water	45.40	45.40
Slip agent	0.20	0.20
In-can preservative	0.10	0.10
Pseudoplastic HEUR thickener	0.40	0.40
Newtonian HEUR thickener	0.70	0.70
	100	100

putting the water in direct contact for an additional 24 hours. This is rated on a scale of 1-5, with 5 being the best – no changes - and ratings below 2 considered a fail.

Comm ADH and Std ADH samples are taken as benchmarks, setting the minimum performance level for a polymer to be successful in exterior wood applications. As expected, removing ADH from a standard grade without changing the polymer backbone (Std ADH-free in Figures 1, 2 and 3), results in a worse performance overall. ML-745 and ML-747 are as good as Std ADH in presence of No-VOC coalescent to improve film formation. But comparing the polymer films with the solvent-free films shows a clear advantage in the performance of these two newly cross-linked polymers. ML-745-A is lower performing than 745, 747 or the standards. This confirms that the correct combination of the two-phase composition and cross-linker is necessary to get the best results.

**LASURE FORMULATION STUDY**

As the best performing products in the first part of the study, ML-745 and ML-747 were used in the following part of the work and compared in a lasure formulation with commercially available EU Ecolabel prod-

ucts. Two benchmark products from a DIY store were initially characterised to adjust the reference formulation and compare lasures with the same general characteristics. Benchmark products, Ref.A and Ref.B, are glossy lasures, low solids – ranging from 22-23% in weight, and suitable for brush application (specific rheology profile). The formulations ML-19-E and ML-39-D (Table 2), based respectively on ML-745 and ML-747, were used in comparative tests with commercial lasures: block resistance, dry and wet adhesion on bare wood, accelerated weathering, natural exposure.

**BLOCK RESISTANCE**

The lasure samples were applied directly by brush on bare pine wood substrates in three layers:

- > 100 g/m<sup>2</sup> of each layer;
- > 4 hours drying, laboratory conditions, between layers;
- > 16 hours (overnight) drying before block resistance test.

In this test, the coated face is placed in direct contact under a weight pressure for a fixed period of time. In these specific experiments, 1.0 kg/cm<sup>2</sup> weight pressure is applied to one set of samples for 24 hours

Figure 1: No-VOC coalescent influence on polymer block resistance.

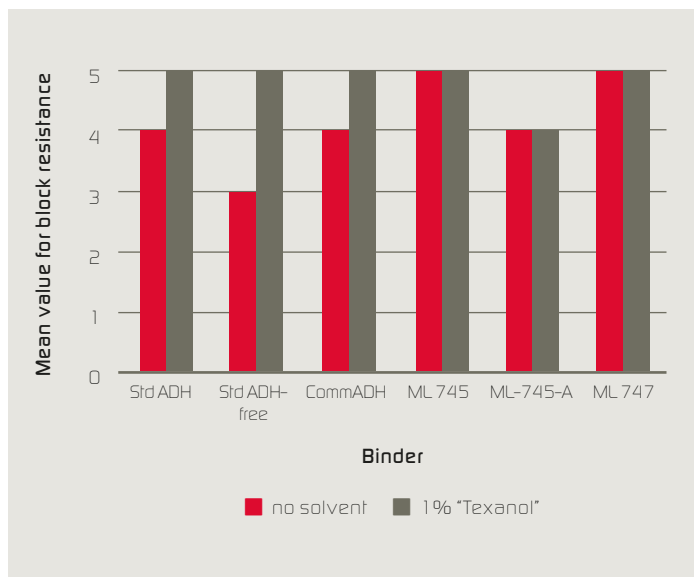


Figure 2: No-VOC coalescent influence on hot block resistance of polymers.

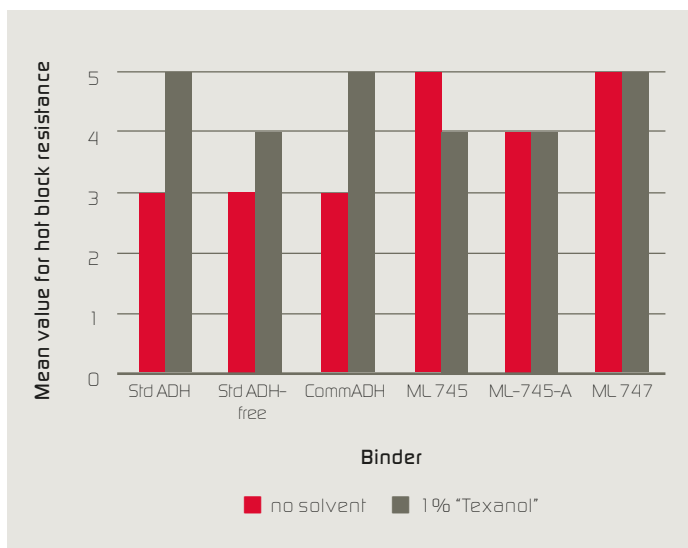


Figure 3: No-VOC coalescent influence on polymer water resistance.



Table 3: Block and hot-block resistance results.

	Ref. A	Ref. B	ML-19-E	ML-39-D
1 hour at 50 °C, weight pressure of 1 kg * 1 cm <sup>2</sup>	5B	5B	5A	5A
24 hours at RT, weight pressure of 1 kg * 1 cm <sup>2</sup>	5A	5A	5A	5A

Table 4: Discolouration after one year of natural exposure.

	ΔL	Δb	ΔE
Ref. A	4.68	6.85	8.37
Ref. B	1.05	4.29	4.61
ML-19-E	0.30	3.78	3.97
ML-39-D	1.04	4.32	5.23

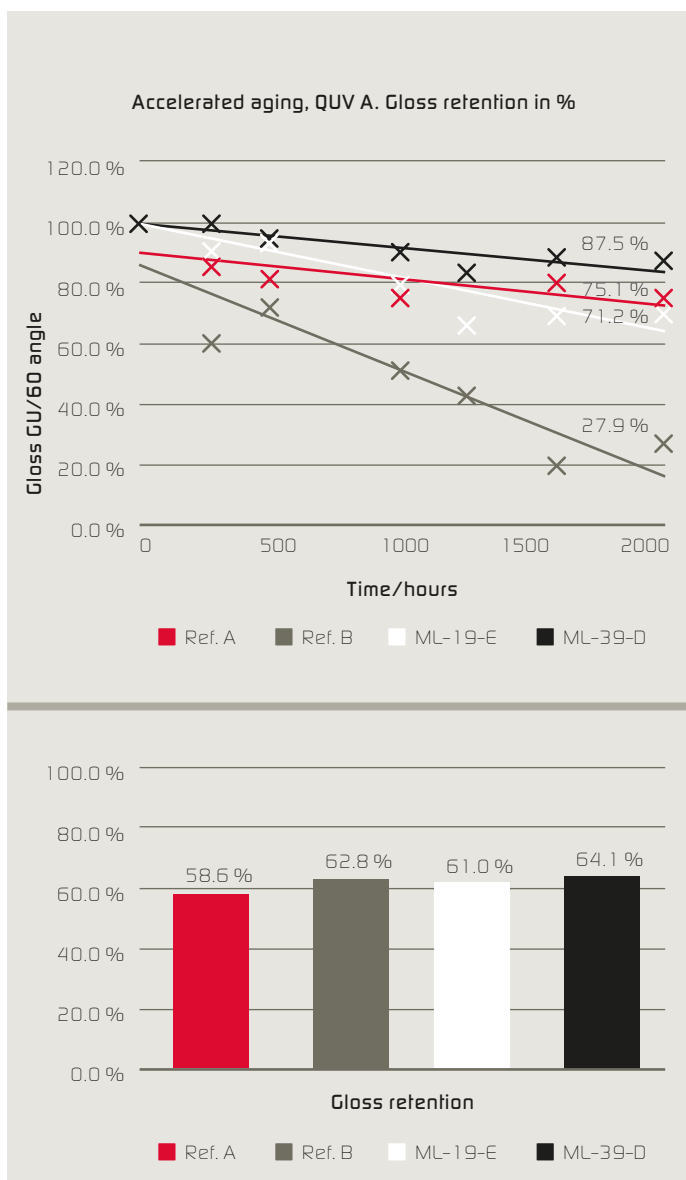
at room temperature and to a second set for 1 hour at 50 °C. Test results are rated on a 1-5 scale, with 5 being the best and rating 1 a complete failure. See *Table 3*.

All the samples show good block resistance, and there is no indication of damage or gloss change in any of the two sample sets. There is only one minimal, non-critical difference between the samples tested for hot block resistance: sample ML-39-D based on Sample 747 fell apart directly when the test piece was checked for damage; sample ML-19-E based on Sample 745 needed to be separated but made no noise; the reference samples made a little 'tac' noise when separated although this caused no damage to the coating film. The minimal difference recorded in hot block resistance can be attributed to different possible causes: solvent type and amount, thermoplastic film, cross-linker used.

### DRY AND WET ADHESION

Adhesion was directly tested on pine wood because lasures are usually directly applied in multiple layers on bare wood. Test formulations were applied in the same numbers of layers and drying conditions of the samples used for block resistance. Adhesion was tested using the

**Figure 4: Gloss retention in accelerated aging test (a) and after one year of natural exposure (b).**



cross-cut adhesion test: cross-cut in the coating film and performance check using a tape; adhesion failure is assessed according to coating removal. Dry and wet adhesion testing differs only in additional step. The cross-cut is covered with water for 1 hour, which is then wiped off and the surface dried with a piece of cloth before applying the tape to evaluate the adhesion. Test results are rated from 0 = failure, removal of >50% of the coating, to 5 = no coating adhesion loss.

Adhesion of the formulations ML-19-E and ML-39-D is generally good and doesn't present any failure in either the wet or dry (rate 5) adhesion, the two commercial references have excellent dry adhesion but one - Ref.B, has lower wet adhesion (rate 3).

### WEATHERING RESISTANCE

The four formulations were glossy lasures. Two key aspects of these types of products are the weathering resistance and the gloss retention, which are evaluated via an accelerated aging test and natural exposure. Accelerated weathering is performed using Q-LAB test equipment, QUV/se, and the samples were exposed for 2000 hours to the following cycle:

24 hours condensation at 45 °C,

5 hours UV-A irradiation (0.89 W/m<sup>2</sup>nm) at 60 °C followed by 1 hour in the dark at 35 °C – repeated 24 times prior to restart with condensation. All the test samples were prepared applying 3 layers on pine wood, as specified previously, and dried for one week under standard conditions before starting the test.

The test gloss is regularly measured and monitored (*Figure 4*) using a glossmeter – TQC GL0030 – and discolouration is measured using a spectrophotometer BYK spectro-guide sphere gloss. The spectrophotometer works in the CieLab colour space and discolouration is measured in delta E, which represents the combination of the variation on the three axes of the CieLab system: L – white/black, a – green/red, b – blue/yellow.

*Figure 4a* shows the gloss retention throughout the accelerated aging test. The ML-39-D formulation is obviously better than the other three. Ref.B shows the worst gloss retention, Ref.A and ML-19-E present acceptable gloss retention, although Ref.A is slightly better than ML-19-E. Discolouration during the accelerated weathering test is minimal and fully aligned for samples ML-39-D and Ref. A, delta E measured after 2000h test is close to 4. Discolouration of the samples ML-19-E and Ref. B is slightly worse and delta E values are higher. Differences in discolouration may be due to substrate failure/change or pigment fading. The four samples were pigmented with the same amount and combination of pigment preparations. We can assume therefore that discolouration is principally due to substrate change and, indirectly, to the protective effect of the lasures.

Boards prepared as described previously, were also subjected to natural exposure on the EPS test fence in the Netherlands. These samples were checked after one calendar year to evaluate gloss retention, discolouration and general appearance.

*Table 4* and *Figure 4b* show the changes after one year of natural exposure. These generally confirm that the performance of the formulations ML-19-E and ML-19-D are at least equal to lasures based on a standard ADH-containing binder. The consistency and confirmation of the results in real-life conditions provides another strong indicator to assess the success of the development. Discolouration following natural exposure of ML-19-E is aligned with ML-39-D and Ref. B while in this case, Ref. A underperforms.

The difference in discolouration after natural exposure or accelerated weathering shows that there is not a 100% linear correlation between the two testing methods and that it is good practice to run both in parallel. After one year of natural exposure, none of the samples show any visual defects such as cracking, flaking or delamination.

*Figure 5* visually summarises the performance of the four tested lasure formulations, showing that ML-19-E and ML-39-D are high performing. ➔

- Moreover, it confirms that the two new acrylic polymers ML-745 and ML-747 are the optimal choice for formulating architectural exterior wood products. The differences between Ref. A and Ref. B remind us of the formulation's impact on the final lasure performance. Binders specifically designed for exterior application are needed to support formulators in getting a successful varnish or lasure with real-life durability.

### NEW POLYMER OFFERS ECOFRIENDLY SOLUTION

The purpose of this study was to invent a new acrylic polymer with low MFFT and ADH-free offering comparable or better performance than standard ADH-based polymers used in the architectural exterior wood segment to formulate lasures and varnishes. Both goals are achieved by using an optimised polymer backbone and cross-linker. The selected products ML-745 and ML-747 offer an EU Ecolabel-compliant solution for exterior wood coatings that are free from environmentally hazardous components whilst retaining high durability of the finished coating. Ⓞ

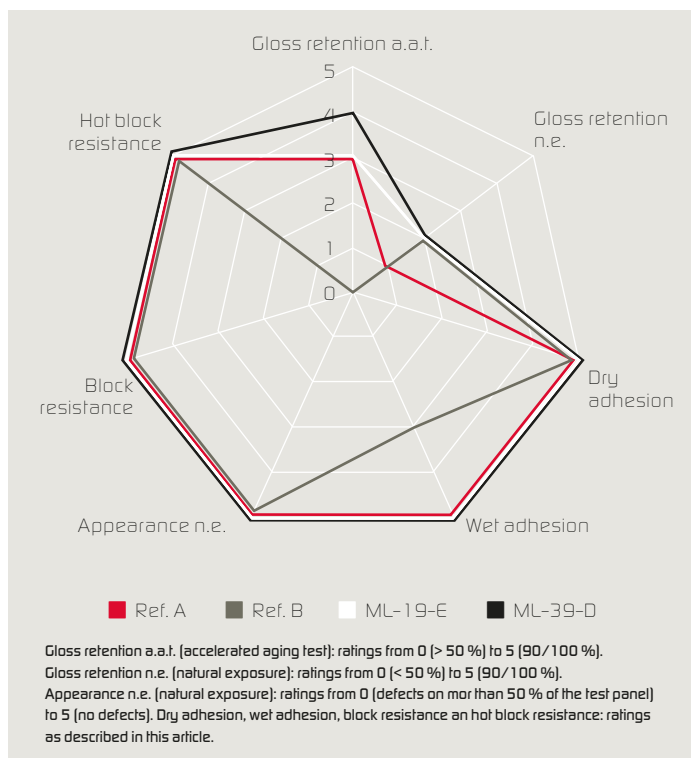
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Figure 5: Overall comparison of the four tested lasure formulations.



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“Colour deviation is a very difficult topic.”

### 3 questions to Massimo Longoni

**In how far does the monomer composition of ML 745 (harder phase) influence the low block resistance at 50 °C with 1% “Texanol”?** In two-phase acrylics the block resistance is definitely influenced by the hard-phase and ML 745 behaviour reflects this concept. The two phase composition is fine-tuned, so that the film formation is optimal without any addition of coalescing agent and the hot block resistance is perfect. The introduction of “Texanol”, that is a no-VOC coalescing agent with a high boiling point and slow release, can plasticise the polymer film in such extent that the block resistance at 50 °C with 1% “Texanol” is inferior to the block resistance without it.

**Is the significant colour deviation of ML-39-D related to the modified cross-linking of ML-747 or to the modified monomer composition?** Colour deviation is a very difficult topic and referring to the study in the article we have not identified any direct correlation with monomer composition or cross-linking. If we look at the results of the accelerated weathering and natural exposure tests ML-39-D performs well in both and better than references A and B that are worse in one test or the other. If I take a step back and look critically at all the formulations' results there is no evidence of which is the key factor in colour deviation between monomer composition, cross-linking and formulation.

**Does the improved gloss retention of ML-39-D result from the modified cross-linking of ML-747 or from the modified monomer composition?** ML-39-D formulation is based on ML 747 that contains a cross-linker, no ADH or other carbodihydrazide, that is not in use in ML 745. If we compare ML-39-D and ML-19-E (formulation based on ML 745) the cross-linker probably plays the mayor role in the different gloss retention performance. ML 747 is the outcome of an incremental improvement process which results in an two phase acrylic that combines optimised composition and cross-linking which are both contributing to match or overcome gloss retention of reference formulations based on ADH containing acrylics.