Study of coatings based on polyisocyanates of moisture cure depending on its resins and water scavengers

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Author: Héctor Farràs Gutiérrez

Director: Rubèn Palomo Ribell

Tutor: Elaine Armelin

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Abstract

Hempel Coatings Company have into products assortment a group of paints which is based on isocyanate pre-polymer resins which cure with moisture forming a coating based on polyurea. These paints are called 1 component polyurethanes (1K PU) or moisture curing polyurethanes (MCU).

The principal function of these paints is the protection of substrates providing durability to the assets. This project was proposed by Protective Coatings R&D Department due to two reasons:

- The resins and water scavengers used for 1K PU are used only for these products so it is really important to have as reduced raw materials stock as possible. In addition these coatings represent a small percentage of the overall Hempel's Coatings production.
- Recently REACH (Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals) has included all the products containing MDI isocyanate monomer/oligomer in the risk sentence R40, limited evidence of a carcinogenic effect, and two 1K PU coatings existing in Hempel contain this isocyanate.

Thus this project was thought to study the isocyanate resins and water scavengers available in Hempel's raw materials stock to reformulate the existing products. When reformulating the existing products the aim is improve 1K PU performance, reduce raw materials stock and, if possible, avoid the use of MDI isocyanates.

The project planning consists of the reformulation of all the possible alternatives of the existing standard products using the raw materials available. Afterwards the products formulated must be produced by vacuum dissolver in order to avoid the moisture incorporation. Finally these products have to be applied on the panels for the final testing. The main properties that 1K PU products need to present have been tested and the best combination of isocyanate resins and water scavengers should be found out.

Summary

Glossary

SVR: Solids volume ratio

MDI: Diphenylmethane diisocyanate

TDI: Toluene diisocyanate

HDI: Hexamethylene diisocyanate

TMXDI: p-Tetramethylxylene diisocyanate

NCO: Isocyanate functional group

1K PU: 1 component polyurethane (moisture cure polyurethane)

MCU: Moisture cure polyurethane

2K PU: 2 components polyurethane

VOC: Volatile organic compounds

CS 10: Abrasion type wheel. (Smooth abrasion)

UV: Ultraviolet rays

NDFT: Nominal dry film thickness

DFT: Dry film thickness

WFT: wet film thickness

pTSI: p-toluene sulphonyl isocyanate

TEOM: Triethylorthoformiate

ASTM: American standard of testing materials.

ISO: International organization of standarization

UNE: Spanish standard (Una Norma Española)

PVC: Pigment volume concentration

Ri: Rusting index.

KU: Kreb Units.

BK: Beck Koller Drying time measure method.

R40: Risk sentence: Limited evidence of carcinogenic effect.

REACH: Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals

Memory core

1. Introduction

Hempel A/S has in assortment two 1K PU (1 component polyurethane) named MCU Primer and MCU Intermediate Coat.

- MCU Primer is a primer coating which contains zinc dust as anticorrosive pigment and micaceous iron oxide as barrier pigment, abrasion resistance and recoating helper. Its main properties are cathodic protection for underground painted pieces, mechanical protection and excellent adhesion to difficult substrates. It is recommended for medium to severe corrosive areas and as a primer for steel substrates in epoxy and polyurethane systems.

- MCU Intermediate Coat is an intermediate coat with high content of micaceous iron oxide. The main properties are high resistance to atmospheric and mechanical exposure. It is recommended for severe corrosive atmospheres and as part of 1 component polyurethane systems or epoxy and 2K PU (2 component polyurethane) systems. Railways, bridges and highway are common applications.

Both products have exclusive resins and water scavengers that are not used in any other product of Hempel assortment. Besides both 1K PU are affected by REACH (Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals) since June 2009. The products with content above 1% of MDI (Diphenylmethane diisocyanate) must be labeled with the risk sentence R40: Limited evidence of carcinogenic effect.
The study of the performance of these raw materials in the 1K PU will help us to know if substitution and reduction of them is possible.
Several alternatives to the actual standard formulas were developed in order to check the influence of different combinations of water scavengers and resins in final paint film.

1.1. Study case goal

The main aim of this study is to formulate the best quality, production cost and environmental friendly Hempel moisture cure polyurethane coatings as possible.

1.2. Study case plan

First of all the raw materials available in Hempel's stock plus some raw materials available in the market must be studied in order to have an overview of the possibilities to reformulate the existing moisture cure polyurethanes paints.

Then using the raw materials combinations selected all the alternatives to standard formulations which we want to test must be formulated.

When the alternative formulas have been already formulated is necessary to manufacture them in the laboratory.

Finally standard products plus the experimental formula products have to be tested according to the features of each coating. However there are standard quality control parameters which are common parameters for all paints produced. These parameters are: viscosity, density, sagging and stability.

Then specific parameters must be checked depending on the function of the product. In the moisture cure polyurethanes of Hempel:

- MCU Primer must accomplish the best results in corrosion, abrasion resistance, hardness, impact, flexibility, adhesion and drying time.
- MCU Intermediate Coat must accomplish the best results in corrosion, abrasion resistance, hardness, impact, flexibility, adhesion, drying time and UV resistance.

1.3. MCU Primer standard formula resins and water scavengers

MCU primer standard formula contains isocyanate prepolymers resins based on MDI and TDI (Toluene diisocyanate) homopolymer or homoligomer. All the water scavengers available in Hempel's stock are used: MDI based, pTSI (p-toluene sulphonyl isocyanate) based and triehtyl orthoformiate based.

1.4. MCU Intermediate Coat standard formula resins and water scavengers

MCU Intermediate Coat standard formula contains isocyanate prepolymers based on TDI and MDI hompolymers. Highly reactive water scavengers are used to avoid moisture reacting with the resin during manufacture process: MDI and pTSI based.

1.5. Resins and water scavengers available for the study

The isocyanate resins and water scavengers available for 1K PU in Hempel were studied.

- **Aromatic isocyanates (Useful for primer and intermediate coatings)**

1. Resins based on MDI (R40-toxic)

E152: High anticorrosive power, very high surface tolerant, high viscosity: 5400mPa·s. [1]

E231: High anticorrosive power, low VOC content. Low viscosity: 1800 mPa·s. [1]

2. Resins based on TDI (Aromatic alternative to MDI)

E155: The main alternative to MDI. It has very remarkable anticorrosive properties, low tendency to yellowing in high thickness films and fast drying but high VOC and poor surface tolerance. It can be used as topcoat when it is aluminum pigmented. [1]

E156: Used as plasticizer. It is not used as a unique resin in formulation, but as a complement of harder resins. [1]

E232: It is not common, is very brittle and weak as anticorrosive. It is not a real alternative. [1]

TDI or MDI based binder are recommended for primer or intermediate coatings, the main differences between them are:

- TDI: Offers faster physical drying, less carbon dioxide bubbling problems and better recoating adhesion after weathering. But has lower solids content, requires blasted surface (roughness), more brittle film formed.
- MDI: Offers 100% solid resins, possible to use in difficult surfaces (without roughness). Due to lower vapour pressure than TDI it has better adhesion properties. [2]

3. Water scavengers based on aromatic isocyanates

D755: Highly reactive isocyanate, must be added in grinding step of manufacture process, is based on MDI monomer. [1]

D508: Similar performance to D755. It has good water scavenger properties because of the fast water reaction and it is based on pTSI. It has also applications in other coating segments as stabilizer. It is not R40 but it is considered toxic depending on the dose. D508 water uptake is shown in figure 1. [1]

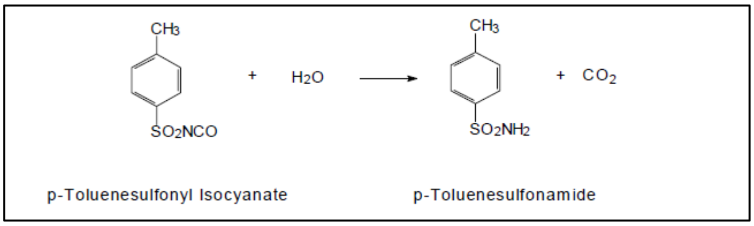


Figure 1: D508 water reaction.

D509: Used to scavenge the water in the storage conditions and added in let down. It is based on triethylorthoformiate (TEOM) which is less reactive than the previous mentioned water scavengers. [1]

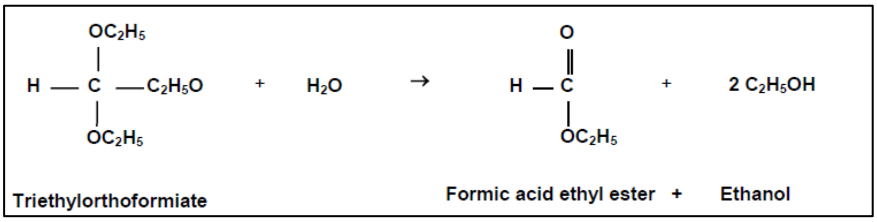


Figure 2: D509 water reaction

- **Aliphatic isocyanates (useful for topcoat coatings)**

1. Resins based on HDI (hexamethylenediisocyanate)

HDI-R: This product is used for topcoats which require high gloss and UV resistance because its aliphatic structure. [1]

2. Water scavenger for aliphatic isocyanates

HDI-WS: It is the water scavenger recommended for HDI-R, is based on HDI isocyanate. [1]

Table 1 shows the summary of isocyanate resins available in Hempel for 1K PU.

Table 1: Resins for 1K PU theoretical information.

Resin	Isocyanate monomer	Solids in weight (%)	NCO (%)	Viscosity (mPa·s)	Equivalent weight (g/eq)
E152	MDI	100	16	5400	263
E155	TDI	61	6.8	500	618
E156	TDI	100	3.3	6800	1273
E231	MDI	100	15.4	1800	273
E232	TDI	60	5.3	1800	792
HDI-R	HDI	70	10	1400	420

Table 2 shows the summary of water scavengers available in Hempel for 1K PU.

Table 2: Water scavengers for 1K PU.

Resin	Base	Solids in weight (%)	NCO (%)	Viscosity (mPa·s)	Equivalent weight (g/eq)
D755	MDI	100	16.8	900	250
D508	pIST	100	20	54	210
HDI-WS	HDI	100	11.8	75	356
D509	TEOM	100	-	125	-

Equivalent weight relation with NCO proportion:

$$\boxed{Equivalent\ weight\ \left[\frac{g}{eq}\right] = \frac{NCOgroup\ weight\ \left(\frac{g}{mol}\right) \cdot 100}{\%NCO}}$$

NCO group weight is 42g/mol.

Figure 3: Equivalent weight calculation.

1.6. 1K PU alternative formulas studied

1.6.1. MCU Primer alternatives

MCU primer coating was reformulated with two combinations of resins and water scavengers different from the standard. One alternative was thought as resins modification and the other one as resin and water scavenger modification and thus MDI free alternative. Figure 4 shows the resins and water scavengers used.

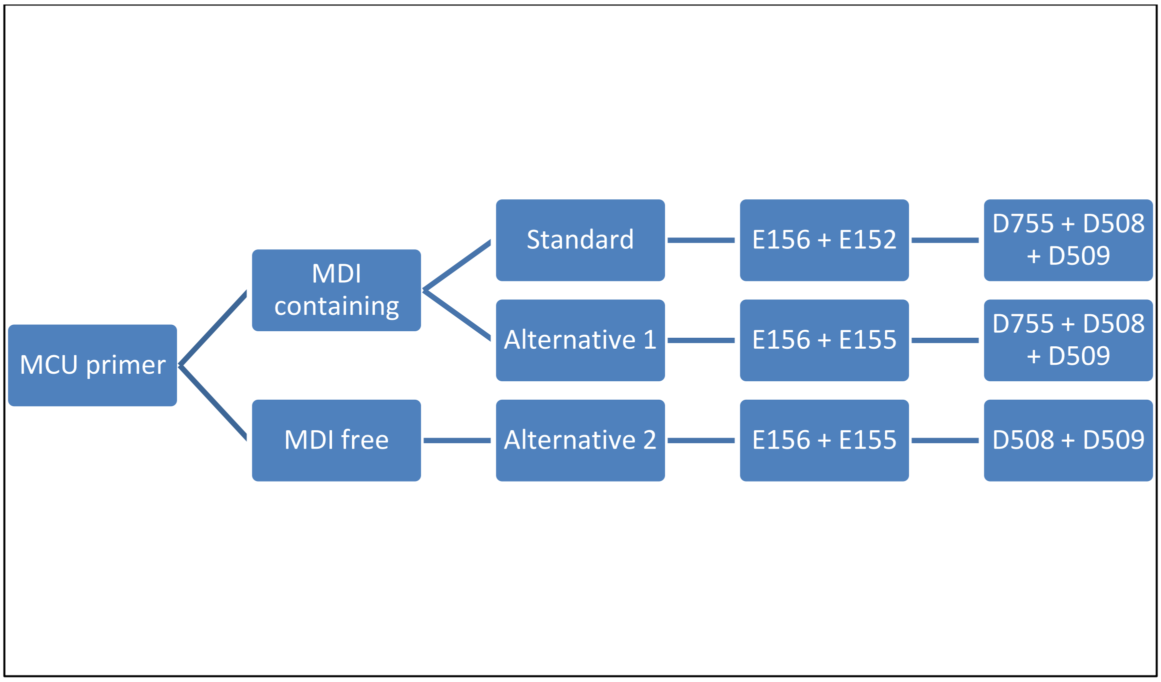


Figure 4: MCU primer formulas diagram

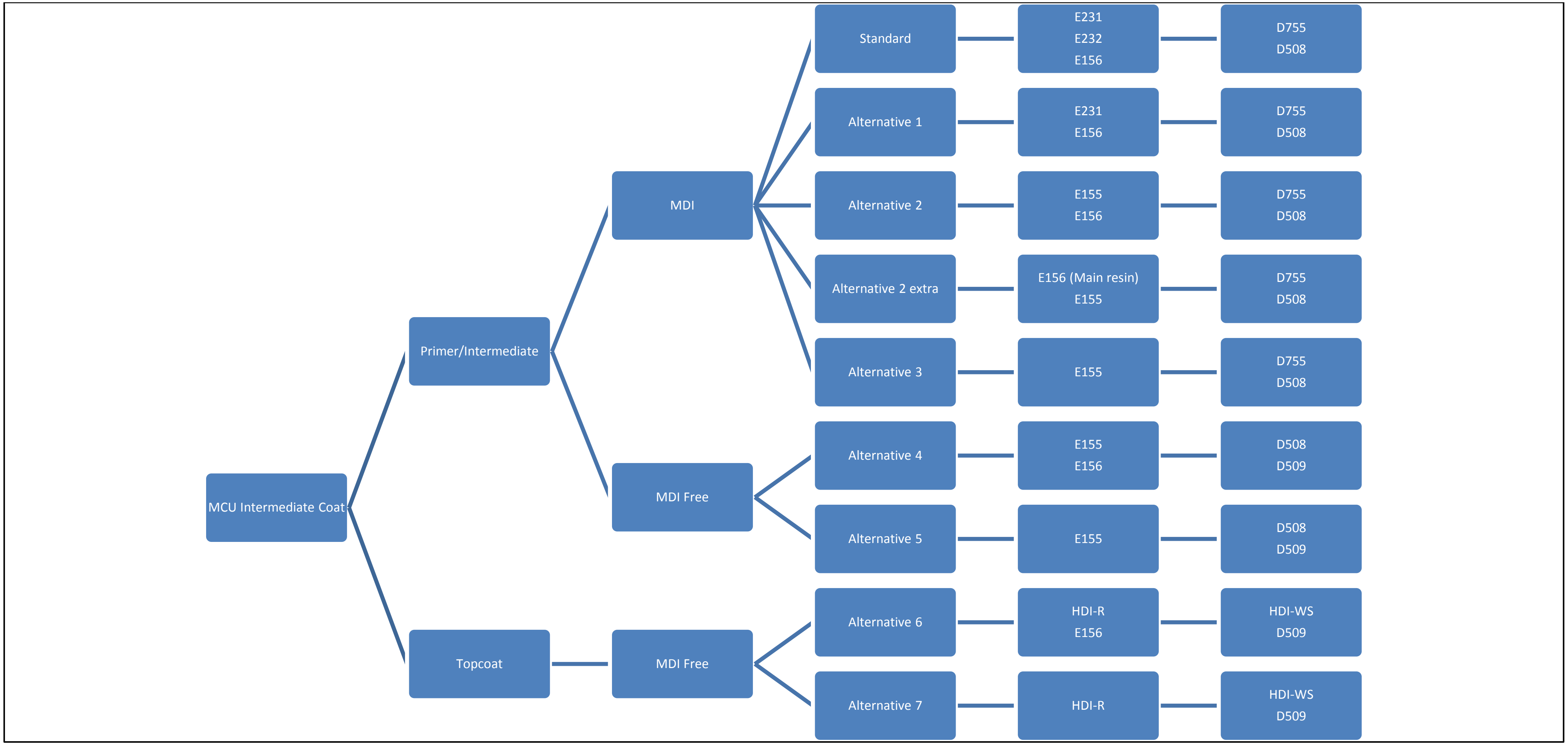
As alternatives we do not take into account E152 because it has low anticorrosive properties, it gives brittleness to the film and it is not a common resin. Instead of this resin, E155 with E156 is proposed because E155 has good anticorrosive and hardness properties and on the other side, E156 gives the flexibility properties that a zinc primer needs.

For water scavengers there is the MDI free alternative: D508 with D509. Two water scavengers are used because they play different roles in the water scavenge of the paint.

1.6.2. MCU intermediate coat alternatives

Figure 5 shows the experimental formulas to find the best MCU Intermediate Coat as intermediate coating and as possible topcoat.

Figure 5: MCU intermediate coat experimental batches diagram.



MCU Intermediate Coat alternative formulas could be classified depending on the purpose of the coating. If the coating is kept as intermediate coat the alternative formulas vary the resins and water scavengers giving all the possible substitutions with aromatic isocyanates. If the coating is modified for topcoat purpose then there are more alternatives based exclusively on aliphatic isocyanates. Inside this two categories there could be formulated MDI containing or free.

1.6.3. Formula substitution calculations

The replacement of isocyanate resins in the experimental formulas consisted on keep the same amount of solid resin. In this way we can compare solid amount per solid amount of alternative resin. On the other hand the replacement of water scavengers was based on the number of isocyanate moieties. Table 3 shows the relations used.

Table 3: Experimental formula replacements.

Replacement in formula	Relation
E152 to E155	$\mathrm{E155} = \mathrm{E152} * \frac{100\%\mathrm{solids}}{61\%\mathrm{solids}}$
E231 to E155	$\mathrm{E155} = \mathrm{E231} * \frac{100\%\mathrm{solids}}{61\%\mathrm{solids}}$
E232 to E231	$E231 = E232 * \frac{60\%\ solids}{100\%\ solids}$
E232 to E155	$\mathrm{E155} = \mathrm{E232} * \frac{60\%\mathrm{solids}}{61\%\mathrm{solids}}$
E156 to E155	$\mathrm{E155} = \mathrm{E156} * \frac{100\%\mathrm{solids}}{61\%\mathrm{solids}}$
E231 to HDI-R	$\mathrm{HDI.R} = \mathrm{E231} * \frac{100\%\mathrm{solids}}{70\%\mathrm{solids}}$
E232 to HDI-R	$\mathrm{HDI.R} = \mathrm{E231} * \frac{100\%\mathrm{solids}}{70\%\mathrm{solids}}$
D755 to D508	1:2 (w/w) (diisocyanate to monoisocyanate)
D755 to HDI-WS	1:1 (diisocyanates)
D508 to HDI-WS	2:1 (monoisocyanate to diisocyanate)

*The amount of D509 added in the modified formulas was 12.5% of D508 amount as indicated in the technical data sheet of the raw material.

When any formula was modified deleting a resin the amount of this resin was transfered to the other resins according to the ratio resin to resin of the original formula. In this way we keep the resins ratio and the effect of the resin elimination is comparable.
For instance in MCU intermediate Coat alternative 1 which is exactly the same formula as standard but without E232, the amount of the mentioned resin has been transferred to E231 and E156 in different grades depending on the ratio between them. If E231 is 90% and E156 is 10% of total resin system, E231 receives 90% the amount of E232 resin present in standard.

2. Materials and methods

2.1. 1K PU production

The paint manufacture processes of coatings which not require fineness below 30 microns takes place in high speed dispersers. In the case of moisture cure polyurethanes the dispersion of raw materials must take place in vacuum high speed dissolvers to avoid moisture stability problems.

Figure 6: Vacuum dissolver used for the experiment (Hempel Denmark Lab south)

The vacuum dissolver consists of disperser with a vacuum pump wired to it.

Figure 7: Vacuum pump is allocated side by side to the manufacture tin container.

The vacuum pump suctions the air of a big container made of teflon which contains inside the manufacture tin. Once the container cover is fixed on the pump acts and reduces the pressure inside.

Figure 8: Vacuum dissolver display.

Figure 8 shows the control panel of vacuum dissolver. Linear dispersion speed, scraper action, dispersion temperature and shaft height are the main parameters to control during paint production.

2.1.1. Manufacture of MCU Primer

The manufacture of the most common protective paints contain the same steps as MCU primer:

1. **Premix**: Resins and solvents are mixed during short time (5 to 10 minutes) to have low viscosity polymer matrix.
2. **Grinding/Dispersing phase**: All the pigments and fillers are added to the mix and must be grinded until reach the fineness required for that product or reach the temperature required for special additives activation. In the case of MCU primer we needed to wait until 55ºC and then keep the temperature during 15 minutes to activate a special rheological agent.
3. **Let down:** The rest of resins, solvents and additives are added during 10 minutes mixing.

However due to the fact that this dissolver has never been used before this project some difficulties in initial productions were observed.

In the second step when 50ºC were reached under vacuum the solvent started to evaporate and it condensed in the walls of the vacuum dissolver container. The vacuum dissolver of Denmark R&D consists of a big tank which contains inside the open production tin. The design of this machine has the handicap of condensation of solvent vapours out of the production can. Thus in the final can the amount of solvent has decreased significantly. In this specific production the final product was too viscous to be accepted.

The solution found in order to avoid the loss of solvent content consisted on apply the vacuum just 3-5 minutes to remove the whole moisture in the beginning of each step. After this, we reach again the atmospheric pressure but keeping the tank closed. Then the moisture inside is minimum.

In the second batch of production of the same product there was another problem. The temperature measurement was not correct and then the production batch reached too high temperatures (around 100ºC). The method of temperature measurement is based on IR rays, therefore is possible to measure the temperature in the surface but not in the centre of dispersion mass. In this case during the manufacture process the indicator did not show more than 34ºC but taking a sample and measuring it with normal termometer the temperature was 98ºC. We concluded that in next manufactures we needed to deep into the production mass a normal termometer.

Then after the problems exposed in the first experimental batches we explain the final procedure followed:

1. Mixing during 5-7’, the first 3’ must be under vacuum (0.025atm). Speed of 800 rpm.
2. Grind (20 m/s) until reach 55-60ºC, during the first 3 minutes vacuuming, then stop vacuum and keep the tank at atmospheric pressure with no transfer of air. Measure the temperature often. Keep at 60º C during at least 15-20minutes.
3. Let down during 10 minutes with 3’ vacuum.

Operational data in the laboratory:

Table 4: MCU primer operational data.

Step	Phases	Time (minutes)	Pressure (atm)	Grinding speed (rpm)	Temperature (ºC)
1	1	3	0.025	800	25-30
	2	3	1 (+ pressure due to the		

			heat)		
2	1	3	0.025	1000	30 to 35
	2	6	1	3000-3500 (20m/s)	35 to 55-60
	3	20		1000	55-60
3	1	3	0.025	800	40-45
	2	3	1		

2.1.2. Manufacture of MCU Intermediate Coat

It is divided in 3 parts:

1. 3 minutes mixing under vacuum and 2 minutes more mixing at 800rpm obtaining a gel (bentone clays are used as thixotropic agents and they must swallow).
2. Grind during 3 minutes at 1000 rpm till reach 40-45ºC with vacuum. After this, increase the speed until 4000 rpm (20-21m/s) and keep it during 6-7 minutes reaching 55-60ºC. Then keep the temperature grinding at 2000 rpm.
3. Let down during 10 minutes at 800 rpm, the first 3 minutes under vacuum

Operational data in lab:

Table 5: MCU intermediate coat operational data.

Step	Phases	Time (minutes)	Pressure (atm)	Grinding speed (rpm)	Temperature (ºC)
1	1	3	0.025	800	25-30
	2	3	1 (+ pressure due to the heat)		
2	1	3	0.025	1000	30 to 40-45
	2	6	1	4000 (20-21m/s)	40-45 to 55-60
	3	20		2000	55-60
3	1	3	0.025	800	40-45
	2	3	1		

- Observations of batches produced
    - All the paints once packed are dangerous to open. The pressure of the air inside the can is higher than atmospheric, so it has to be opened carefully with protection.
    - Just the alternative 1 presents difficult to be mixed manually in order to apply. It needs mechanical shearing to reach good rheology.

- E232 decrease the viscosity of the paint which makes easier application, nevertheless this means a decrease of sagging result.
- E156 seems to have no influence in viscosity or sagging.
- HDI resins make the best rheology (low viscosity when applied).

- Problems in alternative 2 batch

Sagging results of MCU Intermediate Coat standard and alternative 2 have not been good enough, we reheated the sample until 60ºC and kept it for 30 minutes. The results of sagging afterwards were:

- MCU Intermediate Coat standard: sagging 25 mils. It fits into quality control parameters.
- MCU Intermediate Coat Alternative 2: sagging: 10 mils. Too low for the product.

As the alternative 2 did not improve sagging after oven, it was necessary to produce another batch. This new alternative is called Alternative 2 extra and it contained different resins ratio.
Alternative 2 extra contained E156 at higher levels than Alternative 2. In order to know the amount of E156 respect E155 in the formula we used the solid content of each resin.
Table 6 shows the comparison between alternative 2 and the new alternative.

Table 6: Alternative 2 and 2 extra resins content.

Product	Resins	% (w/w) solid resin respect total paint
MCU Intermediate Coat alternative 2	E155	15.7
	E156	4.9
MCU Intermediate Coat alternative 2 extra	E155	5
	E156	15.5

2.2. Tests

2.2.1. Quality control parameters

2.2.1.1. Viscosity

Oscillating rheometer (viscosimeter) measures the dinamic viscosity of the product in Krebs Units (KU) using shearing force.
The viscosity was measured after 2 minutes shearing the paint at 2000 revolutions per minute due to the thixotropy.

Figure 9: Stormer rheometer.

2.2.1.2. Specific gravity

Density was measured in pycnometers of 100 cm^3. First the pycnometer needs to be tared, afterwards it has to be filled complete by paint if it has no air content. Finally it is obtained the weight of paint per 100cm^3 which has to be converted to g/cm^3.

Figure 10: Pycnometers.

2.2.1.3. Sagging

Sag test method is intended for evaluation of the tendency of a paint to form sags or runs when applied and left to dry on a vertical non-absorbing substrate at specified film thickness.

The test consists on applying different film thickness of paint over a non absorbing panel by a anti-sag leneta. (figure 11)

Figure 11: Anti-sag leneta.

Immediately after applying the stripes of paint at different film thicknesses the panel needs to be positioned vertical. The sagging index will be the maximum wet film thickness applied wich formed a stripe on the panel without touching the next stripe. The film thickness is worlwide measured in mils units (1mil equal to 25microns).

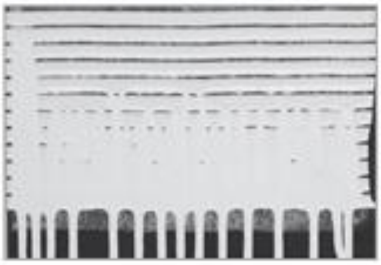


Figure 12: Sagging resistance.

2.2.1.4. Drying time

Beck Koller measurer for drying time of coatings consists of needles which make pressure over recent painted glass stripes, painted at a exact wet film thickness. These needles slide over the paint at precise speed. Depending on the paint drying time the speed of the needle slide can be changed. Because of needle pressure the paint film is broken when it is wet, scratched when is curing and it has no deffect on the surface when it is fully cured. The transition between broken film and scratch determines BKIII time which is considered as drying time of the paint.

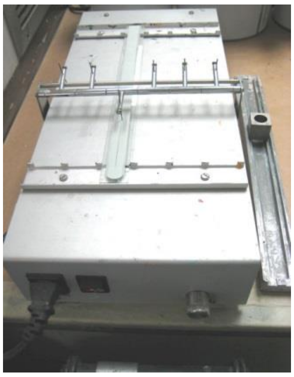


Figure 13: BK drying time recorder working. On the right side of the machine there is the applicator.

2.2.1.5. Stability test

The stability checked in this project consisted on measuring control parameters: viscosity and sagging one month after manufacturing the coatings.

2.2.2. Specific parameters

2.2.2.1. Anticorrosive resistance – Neutral Salt Spray Test

According to ISO 9227, neutral salt spray is performed in order to assess the corrosion resistance of metallic materials coated with organic protection. The operation conditions of the salt spray test are constant spray with 5% NaCl solution at 35°C.

At the selected inspection intervals during and after completion of exposure blistering and rusting are evaluated on the panels. These panels contain a scribe line in one side (line which exposes steel substrate without coating). The rust creep away of this score is the most important parameter to evaluate. Other parameters evaluated are cracking and delamination according to ISO 4628.

In the project rusting, cracking, flaking, blistering after some time periods were checked and after the whole test time corrosion from scribe line was evaluated.

Corrosion of the substrate from the scribe line shall be calculated using following equation:

$$Mavg = (C - W)/2$$

Figure 14: Rust creep evaluation equation.

Where C is the average of nine width measurements and W is the original score width in millimetres. Mavg is corrosion creep average. Only one of the three test panels shall be allowed not to comply completely with the requirements (usually less than 1 mm).

2.2.2.2. Abrasion resistance

According to ASTM D 4060 wear or abrasion resistance is determined applying Taber Abraser. Abrading wheels of determined weight rotate at constant speed over the coated panels until complete the rotations required for that coating. The wear-index is given as weight loss/ rotations. The temperature and humidity during testing are 23°C and 50% relative humidity. Wheel type and load are recorded in the report.

In the project the rotations vary depending on the coating that we are measuring. MCU Primer after 100 rotations has been completely weared whereas MCU Intermediate Coat is still coating the panel. The wheel type and the load were: CS10 wheel which is the less abrasive wheel and the load was the standard of 1000g per wheel.

Figure 15: Taber tester.

2.2.2.3. UV resistance – QUV-B Accelerated weathering test

According to ISO 11507:97 QUV-B is an accelerated weathering test which uses fluorescent ultraviolet light (UV) and water condensation apparatus to simulate the deterioration caused by sunlight and water as rain or dew. The test cycle consists on 4 hours UV-light at 60ºC with UVA-340 lamps and 4 hours condensation at 50°C for a total of determined hours.

The panels are evaluated for gloss/colour/chalking/cracking during/after exposure according to relevant standard.

For both 1K PU this test was the less important due to the fact that both coatings are not topcoats and contain aromatic resins which we know tend to yellow with UV exposure. However it was interesting to check the differences and after the determinated hours of exposure there were checked colour difference and defects on the surface.

The colour difference was measured by spectrophotometer. The computer compares the colour after exposure with the colour measured before exposure. The total colour difference dE is calculated using equations regarding dL (lightness), dh (hue) and dC (chroma).

Figure 16: QUV-B tester.

2.2.2.4. Adhesion – Cross-cut test

According to ISO 2409 this method is performed in order to estimate the adhesive and cohesive strength of a coating system. A cross-cut at approximately 35° angle is done through the film to the substrate. Pressure sensitive tape is applied over the cut and rubbed firmly before it is pulled at once. The adhesion rating is evaluated by comparing to the rating pictures from the norm.

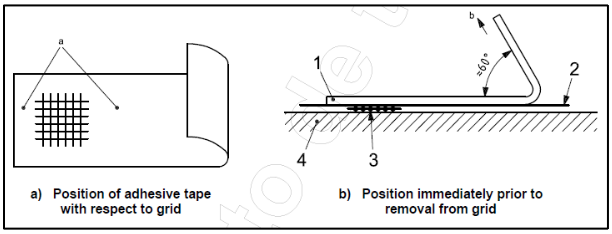


Figure 17: Graphic explanation of Cross-cut test

Table 1 — Classification of test results

Classification	Description	Appearance of surface of cross-cut area from which flaking has occurred (Example for six parallel cuts)
0	The edges of the cuts are completely smooth; none of the squares of the lattice is detached.	—
1	Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not greater than 5 % is affected.	
2	The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area greater than 5 %, but not greater than 15 %, is affected.	
3	The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area greater than 15 %, but not greater than 35 %, is affected.	
4	The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area greater than 35 %, but not greater than 65 %, is affected.	
5	Any degree of flaking that cannot even be classified by classification 4.	—

Figure 18: Adhesion evaluation where 0 is the best result and 5 the worse with the whole coat flaked.

2.2.2.5. Flexibility- Mandrel bend test

According to ISO 1519 the test method consists on place a thin panel coated over a mandrel. Using a steady pressure of the fingers we need to bend the panel approximately 180° around the mandrel. Afterwards the panels must be checked in order to see if there is cracking visible to the eye. If cracking has not occurred, repeat the procedure using a smaller diameter mandrel in untested panels until failure occurs or until the smallest diameter mandrel has been used. The diameter of smallest mandrel not causing failure is reported, the mandrel diameters available go from 2 to 32mm.

Figure 19: Flexibility tester with set of mandrels.

2.2.2.6. Impact resistance – Falling weight test

The effect of rapid deformation is evaluated according to ISO 6272-1 using an Erichsen Impact Tester. This test method covers a procedure for rapidly deforming by impact a coating film and its substrate. The test is performed on 1.5 mm panels. After the coatings have been cured, a falling weight of 1 kg, with an indenter-head of determined diameter, is dropped at a distance of 70cm onto the test panel. When the indenter strikes the panel it deforms the coating and the substrate. By gradually decreasing the weight's diameter, the point at which failure usually occurs can be determined. The impact weight diameter value is reported as the sharpest impact, reproduced 5 times, which results in no visible cracks and no adhesion failure in the paint film.

Figure 20: Impact tester.

2.2.2.7. Hardness – König pendulum test

According to UNE ISO 1522 (ISO 6272) König and Persoz pendulum tests cover the same principle, the widtheness of pendulum oscilation when touching a surface decrease faster when the coated surface is softer. However König and Persoz pendulums are different regarding size, period and widtheness of oscilation and moreover König measures hardness as oscillations and Persoz as seconds oscillating. König pendulum is the one used in this project because is more reliable method due to the fact that with Persoz the pendulum holders can slide over the coating.

Glass panels are painted by blade applicators. The hardness is measured at two different dry film thicknesses in order to get an average result at 50 microns dry film thickness. Then hardness must be measured one day after application, two days, three days, one week and two weeks after.

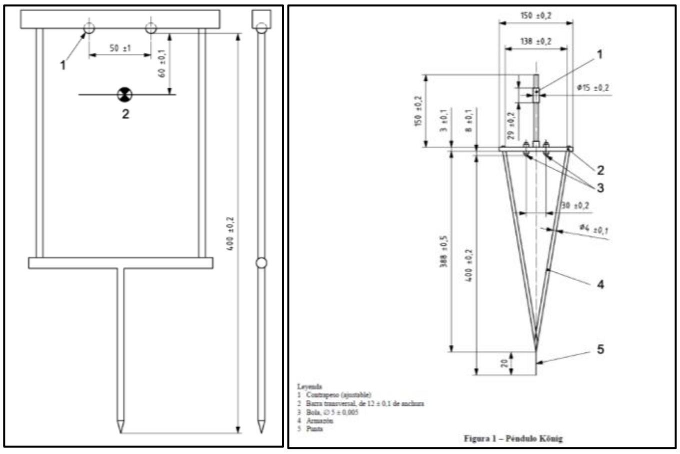


Figure 21: On the left Persoz pendulum and on the right König pendulum. Persoz pendulum starts oscillating at 12º tilting whereas König starts at 6º.

3. Results and discusion

First of all we show the theoretical data of each 1K PU formula tested. This information is the first one obtained once we formulate any product. Product Vision software calculates the properties of the coating according to the data input of each raw material used in the formula.

3.1. MCU Primer theoretical data

The formulas tested of MCU primer had the properties shown in the table 7.

Table 7: Theoretical data of MCU Primer formulas.

MCU Primer	Price	SVR (%)	% NCO groups
MCU Primer standard	STD	66	1.51
Alternative1	STD + 1.7%	65	1.20
Alternative2	2.973 + 20%	69	1.66

The solids content does not vary significantly between the alternatives formulated. On the other hand we obtain the higher percentage of NCO groups and price with Alternative 2.

3.2. MCU Intermediate Coat theoretical data

The formulas tested of MCU Intermediate Coat had the properties shown in the table 8.

Table 8: Theoretical data of MCU Intermediate Coat formulas.

MCU Intermediate Coat	Price	SVR (%)	% NCO groups
MCU Intermediate Coat standard	STD	51	2.13
Alt 1	STD -4%	52	2.53
Alt 2	STD +7%	51	2.00
Alt 2 extra	STD + 11%	55	1.54
Alt 3	STD + 14%	51	2.50
Alt 4	STD + 29%	53	2.43
Alt 5	STD + 36%	53	2.92
Alt 6	-	51	2.18
Alt 7	-	49	2.90

The solids content is kept between 49 and 55% so the formulas are comparable. The higher percentage of NCO groups and price are obtained with alternative 5 formula.

3.3. MCU Primer control data

At least one day after each batch is produced the quality control data needs to be obtained in order to verify if the product was properly produced or not. This is checked by control parameters range of tolerance for each product.

Table 9: MCU primer Coat quality control parameters.

Product	Density (g/mL)	Viscosity (KU)	Sagging (mils)	Drying time BKIII (hours)
Product specifications	2.67-2.77	105-110	16-20	3
MCU Primer standard	2.737-2.767	117	60	2
MCU Primer alternative 1	2.455-2.479	100.9	30	1

MCU Primer alternative 2	2.419-2.424	99.7	25	2

The two alternatives containing TDI resins show a drastic decrease of density values and slightly in the case of viscosity. Drying times and sagging results are correct in all the products. Finally it is important to remark the excellent sagging obtained with the standard which is over the specification.

3.4. MCU Intermediate Coat control data

Table 10: MCU Intermediate Coat quality control parameters.

Product	Density (g/mL)	Viscosity (KU)	Drying time BKIII (hours)	Sagging (mils)
Product Specifications	1.64-1.70	95-105	4	16-25
MCU Intermediate Coat standard	1.641	91.5	0.5	25
MCU Intermediate Coat alternative 1	1.678	97.9	3.5	35
MCU Intermediate Coat alternative 2	1.499	97.7	0.5	10
MCU Intermediate Coat alternative 2 extra	1.565	87.0	8	20
MCU Intermediate Coat alternative 3	1.451	93.2	1	20
MCU Intermediate Coat alternative 4	1.356	95.9	3.5	20
MCU Intermediate Coat alternative 5	1.359	95.0	3	30
MCU Intermediate Coat alternative 6	1.644	97.5	11	60
MCU Intermediate Coat alternative 7	1.662	92.3	11	60

The results of MCU Intermediate Coat control parameters vary significantly. The most important idea which gives us the table 10 is that alternative 2 has too low sagging and alternatives based on aliphatic isocyanate resins and alternative 2 extra need accelerators to be applied.

3.5. Stability test: 1 month

Moisture cure polyurethanes are especially sensitive to atmospheric conditions thus storage stability after 1 month from production is an important parameter to check. In this test the quality control parameters need to be checked again. Nevertheless the way to make more remarkable the stability problems is in spray applications as later on will be shown.

Table 11: Stability test results.

Product	Viscosity of production (KU)	Sagging of production (mils)	Viscosity after 1 month	Viscosity difference (%)	Sagging after 1 month	Sagging difference (%)
MCU Primer standard	117	60	127.6	9,1	60	0,0
MCU Primer alternative 1	100.9	30	126.8	25,7	45	50,0
MCU Primer alternative 2	99.7	25	96	-3,7	35	40,0
MCU Intermediate Coat standard	91.5	25	137.9	50,7	20	-20,0
Alternative 1	97.9	35	112.2	14,6	35	0,0
Alternative	97.7	10	150	53,5	10	0,0

2						
Alternative 2 extra	87.0	20	97.6	12,2	9	-55,0
Alternative 3	93.2	20	108.8	16,7	14	-30,0
Alternative 4	95.9	20	92.7	-3,3	16	-20,0
Alternative 5	95.0	30	96.2	1,3	25	-16,7
Alternative 6	97.5	60	99.8	2,4	14	-76,7
Alternative 7	92.3	60	82.5	-10,6	30	-50,0

The stability results are not very satisfactory. MCU primer alternative 1 increses too much the viscosity, viscosity values over 120 KU tend to give application problems by conventional airspray so the applicator needs to dilute too much the paint. MCU intermediate coat formulas gave even worse results we can say that the only formulas which are acceptable regarding stability would be alternative 1, 5 and 7. The reason to decline the rest of formulas regarding stability (which can be improved using higher water scavenger doses or changing them) is either the high increase of viscosity or high decrease of sagging.

3.6. Specific parameters

The laboratory tests carried out in this part of the study required panels applied by airless or conventional air spray insturments. When a coating must be applied, as some lines above was mentioned, is the moment when is really visible if the stability of the paint was really correct. In the case of this study the paints were applied three months after manufacturing therefore theoretically the conditions should be fine, as MCU coatings have normally six months of shelf life. However the results were more interesting than what theoretically we could expect and some coatings were really a challenge to be applied.

- **MCU Primer conditions to apply by airless spray**

MCU Primer batches required 10% thinner based on methoxypropylacetate. The nozzle used was 0.017” at 175 bar. The application was intended to apply at 80 microns which is the recommended film thickness and 50 microns which corresponds to epoxy primer typical thickness. The wet film thickness applied was 100 and 150 microns.

- **MCU Intermediate Coat conditions to apply by airspray gun**

MCU Intermediate Coat batches were painted by airspray gun because some of them were starting to gel on their surface (3 months passed after their production in laboratory). Therefore some of the batches had just 0.5-0.75 Lt useful. The airspray gun needs less amount of paint to apply thus it was chosen for this application.

The dilution of MCU Intermediate Coat varied significantly between the formulas most of them were applied diluting 5 to 15% with a thinner based on buthylacetate. The wet film thickness applied was around 125-175 microns, therefore dry film thickness: 50-80 microns (as specified in technical data sheets).

- **Products aspect when applied-Stability after 3 months**

Stability after one month shown worrying results but we were not able to apply the coatings until three months after manufacture. The reasons were health and safety issues to transport them from Denmark laboratory to Barcelona. Therefore we found some problems to apply the samples as Table 12 shows.

Table 12: Coatings stability after 3 months.

Product	Aspect
MCU Primer standard	No solids settling-application fine
MCU Primer alternative 1	No solids settling-application fine
MCU Primer alternative 2	No solids settilng-application fine
MCU Intermediate Coat standard	1cm hard layer on the surface, coating started to gel.
MCU Intermediate Coat alternative 1	1cm hard layer on the surface, coating started to gel.
MCU Intermediate Coat alternative 2	1cm hard layer on the surface. The one more reacted.
MCU Intermediate Coat alternative 2 extra	Perfect application.
MCU Intermediate Coat alternative 3	1cm hard layer on the surface, coating

	started to gel.
MCU Intermediate Coat alternative 4	It had to be diluted 5%
MCU Intermediate Coat alternative 5	Perfect
MCU Intermediate Coat alternative 6	It had to be diluted 10%
MCU Intermediate Coat alternative 7	It had to be diluted 5%

3.7. Hardness results

Hardness test is a control of hardness film evolution while film is curing. The hardness measured at two different film thicknesses must be calculated for an average of 50 microns.

3.7.1. MCU Primer Coat hardness

The hardness results obtained with the panels applied at two thicknesses above and below 50 microns were normalized to 50 microns DFT to be comparable to any other coating results.

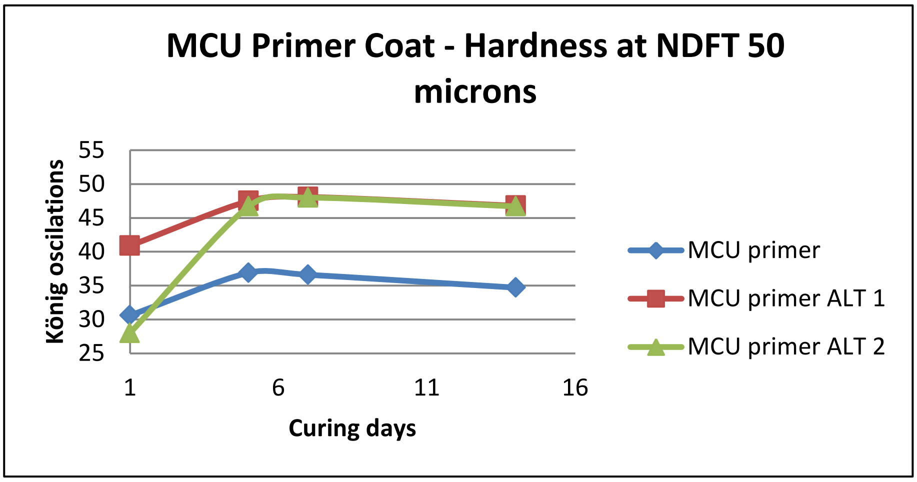


Figure 22: MCU Primer hardness results.

Both alternatives have better hardness performance than MCU Primer standard eventhough alternative two had low hardness beginning.

3.7.2. MCU Intermediate Coat hardness results

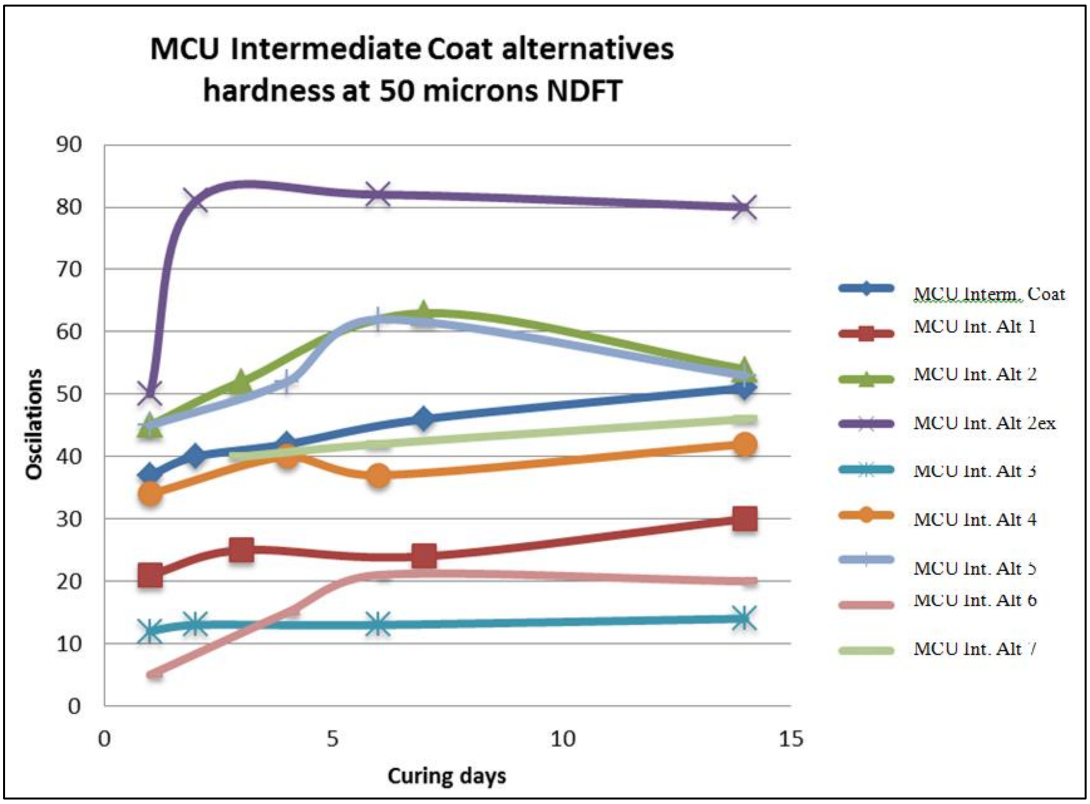


Figure 23: MCU Intermediate Coat hardness results.

Figure 23 shows very interesting results with a wide range of hardness results obtained. If we take standard product as reference above there are three alternatives:

- The two slightly above are alternative 2 and 5
- The highest hardness obtained: alternative 3

These results are very coherent with the raw materials used due to the fact that the flexibilizers E156 and E232 are out of two of these three formulas. Only alternative 2 contains E156.

3.8. Flexibility

The mandrel bend test results are given by the cylinder diameter which bends the panels coated without breaking the film. Therefore results with smaller mandrel means higher flexibility performance.

Table 13: Flexibility test results.

Flexibility results	Cylinder diameter (mm)
MCU Primer	6
MCU Primer ALT 1	8
MCU Primer ALT 2	5

MCU Intermediate Coat	>13
MCU Intermediate Coat ALT 1	6
MCU Intermediate Coat ALT 2	>13
MCU Intermediate Coat ALT 2 extra	<5
MCU Intermediate Coat ALT 3	>13
MCU Intermediate Coat ALT 4	5
MCU Intermediate Coat ALT 5	6
MCU Intermediate Coat ALT 6	8
MCU Intermediate Coat ALT 7	8

MCU Primer flexibility shows that standard formula has high flexibility performance which is just overtaken by alternative 2. This fact could be argumented due the the fact that alternative 2 is based on TDI monomer which is more flexible than MDI. But alternative 1 which gave worse result than standard formula is also based on TDI. Thus the conclusion is that the water scavengers couple of D508 and D509 provides better stability and allows the coating to develop its flexibility more than D755 does.

On the other hand, MCU Intermediate Coat standard has low flexibility results so alternative 1, 2 extra, 4, 5, 6 and 7 have better flexibility. These are very different formulas to be able to take accurate conclusions but there is a very clear conclusion regarding E232. E232 as plasticizer resin has no effect on the coating even the contrary because alternative 1 which is the same as standard but without this resin has improved the performance significantly.

3.9. Cross-cut adhesion

The cross-cut over coated surface according to ISO 2409 must be done by 2mm spacing between cuts when the panel is coated with thicknesses between 61-120 microns. Adhesion over aluminium degreased panels was checked. The aluminium substrate is one of the hardest substrates for coating in terms of adhesion this is the reason to choose it.

Table 14: Cross cut results.

Adhesion Cross-cut results	Level
MCU Primer	0
MCU Primer ALT 1	0
MCU Primer ALT 2	0
MCU Intermediate Coat	5
MCU Intermediate Coat ALT 1	0
MCU Intermediate Coat ALT 2	5

MCU Intermediate Coat ALT 2 extra	5
MCU Intermediate Coat ALT 3	5
MCU Intermediate Coat ALT 4	0
MCU Intermediate Coat ALT 5	0
MCU Intermediate Coat ALT 6	2
MCU Intermediate Coat ALT 7	5

MCU Primer panels adhesion to aluminium substrate was very good in all the batches whereas MCU Intermediate Coat standard and other alternatives shown very low adhesion to this substrate. MCU Intermediate Coat best adhesion were given by alternative 1, 4 and 5.

Cross cut adhesion is not the most important parameter to check on MCU Intermadiate Coat due to the fact that just in small number of applications this coat is applied over pure substrate. Nevertheless is interesting to see how TDI based formulas (4 and 5) can give the same results as MDI based (alternative 1) which theoretically is better for adhesion due to its lower vapour pressure.

3.10. Impact

The weight diameter shows the impact resistance of the film. Smaller dimaters mean higher impact resistance film owns.

Table 15: Impact results.

Impact results	Weight diameter (mm)
MCU Primer	>20
MCU Primer ALT 1	>20
MCU Primer ALT 2	10
MCU Intermediate Coat	15
MCU Intermediate Coat ALT 1	12.5
MCU Intermediate Coat ALT 2	12.5
MCU Intermediate Coat ALT 2 extra	20
MCU Intermediate Coat ALT 3	10
MCU Intermediate Coat ALT 4	10
MCU Intermediate Coat ALT 5	12.5
MCU Intermediate Coat ALT 6	20
MCU Intermediate Coat ALT 7	10

The impact results normally are highly correlated with flexibility results. Table 18 shows MCU Primer standard have very low impact resistance only overtaken by alternative 2 which is the same as we could detect in flexibility test. However MCU Intermediate Coat standard is in the middle of alternatives performance. Taking the standard result as reference the higher results are for alternative 1, 2, 3, 4, 5 and 7, very similar results to what we obtained already with flexibility tests.

3.11. Abrasion

The loss of weight in a coated panel after determined rotations of sandpaper abrasion wheels is the value which allows us to evaluate the abrasion resistance.

Table 16: Abrasion test results.

Abrasion results	Panels	Initial weight (g)	Final weight (g)	Loose of weight 100 cycles (mg)	Loose of weight average (mg)
MCU Primer	1	156.6516	Not weighted	All the paint removed	All the paint removed
	2	155.8872	Not weighted		
MCU Primer ALT 1	1	156.6953	Not weighted	All the paint removed	All the paint removed
	2	156.9140	Not weighted		
MCU Primer ALT 2	1	156.8112	Not weighted	All the paint removed	All the paint removed
	2	157.0436	Not weighted		
MCU Intermediate Coat	1	156.1007	156.0660	34.7	
	2	155.7687	155.7349	33.8	34.25
MCU Intermediate Coat ALT 1	1	155.0502	155.0072	43	
	2	155.5165	155.4735	43	43
MCU Intermediate Coat ALT 2	1	158.3554	158.3432	12.2	
	2	157.8680	157.8537	14.3	13.25
MCU Intermediate Coat ALT 2 extra	1	156.9600	156.9510	9	
	2	156.0346	156.0215	13.1	11.05
MCU Intermediate Coat ALT 3	1	157.0521	157.0305	21.6	
	2	157.6910	157.6685	22.5	22.05
MCU Intermediate Coat ALT 4	1	155.9550	155.9360	19	
	2	155.7137	155.6940	19.7	19.35
MCU Intermediate Coat ALT 5	1	154.9367	154.9150	21.7	
	2	155.7652	155.7458	19.4	20.55

MCU Intermediate Coat ALT 6	1	154.8559	154.7791	76.8	77.05
	2	154.9468	154.8695	77.3	
MCU Intermediate Coat ALT 7	1	154.5898	154.5432	46.6	45.7
	2	155.0498	155.0050	44.8	

MCU Primer abrasion resistance is very low and it could not be measured because after 50 cycles the paint was removed completely from the substrate, something which we could expect because abrasion resistance is not a key parameter for primer coatings.

MCU Intermediate Coat abrasion resistance was measured for 100 cycles with CS10 sandpaper and 1000 grams weight per wheel. The best results of abrasion resistance were obtained by alternative 2, 2 extra, 3, 4 and 5, all of them contain only TDI based resins which corresponds perfectly with the theory.

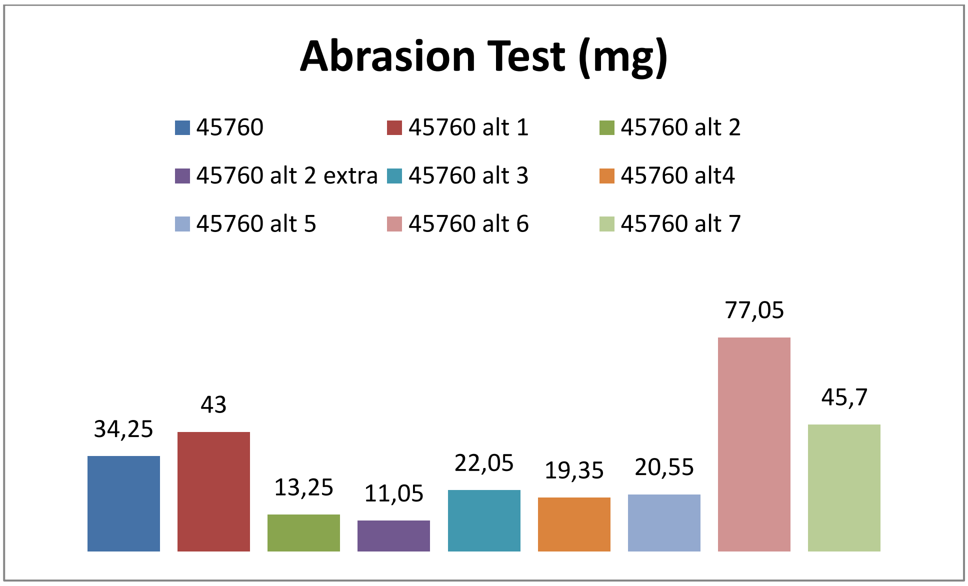


Figure 24: Abrasion test chart.

The 5 formulas containing TDI gave the best results due to the flexibility of this isocyanate compared to MDI.

3.12. Corrosion resistance - Salt spray test

The assessment was done according to ISO 12944-6 and blistering, rusting, cracking and flaking evaluation is according to ISO 4628-2,3,4,5.

Rusting appearance is the most important parameter to evaluate. Figures 25 and 26 show two models of rusting evaluation from ISO12944 and table 17 the percentage of rusting for each Ri (Rusting indicator level).

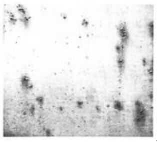


Figure 25: Coating with 1% of rust on the surface is considered as Ri3.

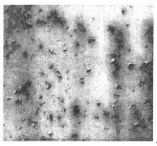


Figure 26: Coating with 8% of rust on the surface is considered as Ri4.

Table 17: Rust classification according to ISO 12944

Rusting degree	Rusted area %
Ri0	0
Ri1	0.05
Ri2	0.5
Ri3	1
Ri4	8
Ri5	40-50

- **Results obtained after 120 hours in salt spray test**

Table 18: Salt Spray Results in panels coated for 120 hours.

DFT (microns)	DFT total (microns)	DFT (microns)	120 hours rusting assessment	120 hours blistering, cracking and flaking assessment	Rust creep 120 hours maximum (mm)	Rust creep average (mm)
MCU Primer-1st Round of panels	MCU Primer standard	65	Ri3	No deffects	<1mm	<1mm
	MCU Primer alternative 1	70	Ri3	No deffects	<1mm	<1mm
	MCU Primer alternative 2	67	Ri3	No deffects	<1mm	<1mm

MCU Intermediate Coat-1^{st} round panels	Standard	120	Ri0	No deffects	<1mm	<1mm
	Alternative1	115	Ri0	No deffects	<1mm	<1mm
	Alternative 2	125	Ri0	No deffects	<1mm	<1mm
	Alternative 2 extra	120	Ri0	No deffects	<1mm	<1mm
	Alternative 3	120	Ri0	No deffects	<1mm	<1mm
	Alternative 4	115	Ri0	No deffects	<1mm	<1mm
	Alternative 5	122	Ri0	No deffects	<1mm	<1mm
	Alternative 6	110	Ri1	No deffects	<1mm	<1mm
	Alternative 7	110	Ri2	No deffects	<1mm	<1mm

With 120 hours exposure we could see no difference among MCU primer coatings. MCU intermediate coat shows good corrosion resistance except with HDI based formulas (alternative 6 and 7).

- **Results after 240 hours in salt spray test**

Another round of panels with MCU primer formulas was applied at higher thickness in order to resist 240 hours.

Figure 27, 28 and 29 show the panels after the exposure.

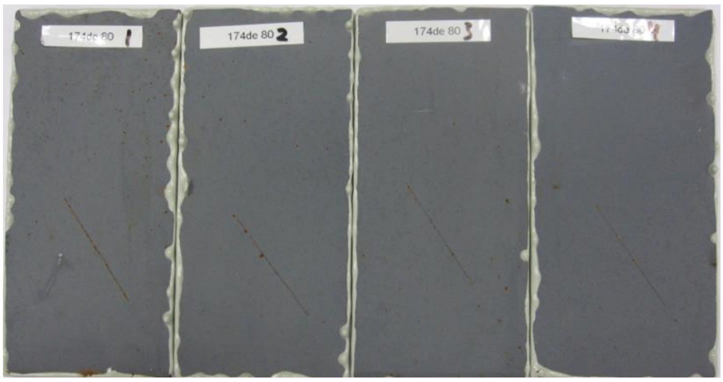


Figure 27: MCU primer standard formula.

In figure 27 the panel 4 has no rusting on the surface but panel 1 is Ri3 and 2 and 3 are Ri2. Therefore the final classification for MCU primer standard is Ri2.

Figure 28: MCU primer Alternative 1.

All the panels of alternative 1 have rust on the surface. Panel 1 and 4 are Ri3 and 2 and 3 are Ri2. We classify MCU primer alternative 1 as Ri 3.

Figure 29: MCU primer alternative 2.

With MCU primer alternative 2 none of the panels have rust on the surface, thus they are Ri0.

Table 19: MCU primer 240 hours results.

Product	Alternative	DFT (microns)	240 hours rusting assessment	240 hours blistering, cracking and flaking assessment	Rust creep 240 hours maximum (mm)	Rust creep average (mm)
MCU Primer-80 panels	MCU Primer standard	125	Ri2	No deffects	<1mm	<1mm
	Alternative 1	120	Ri1	No deffects	<1mm	<1mm
	Alternative 2	135	Ri0	No deffects	<1mm	<1mm

MCU Primer alternative 2 could pass C4-Medium level according to ISO 12944-6 which means that the coating is accepted for high corrosive areas.

- **480 hours (MCU Intermediate Coat)**

The second round of MCU intermediate coat panels coated at higher DFT than the first one obtained the results exposed in table 20.

Table 20: MCU intermediate coat 480 hours results.

DFT (microns)	DFT total (microns)	DFT (microns)	480 hours rusting assessment	480 hours blistering, cracking and flaking assessment	Rust creep 480 hours maximum (mm)
MCU Intermediate Coat-80 panels	Standard	145	Ri0	No deffects	0.4
	Alternative1	140	Ri3	Rusting	-
	Alternative 2	150	Ri0	No deffects	0.5
	Alternative 2 extra	140	Ri0	No deffects	0.4
	Alternative 3	140	Ri0	No deffects	0.3
	Alternative 4	142	Ri0	No deffects	0.2
	Alternative	138	Ri0	No deffects	0.2

	5				
	Alternative 6	135	Ri3	Rusting	-
	Alternative 7	130	Ri4	Rusting	-

All the panels without rusting had less than 0.5 mm of rust creep. Therefore, MCU Intermediate Coat standard, alternative 2, alternative 2 extra, alternative 3, 4 and 5 have passed C4-H, one level above MCU primer result.

Figures 30 and 31 will show the two extremes of MCU Intermediate Coat results for 480 hours salt spray test.

Figure 30: MCU Intermediate Coat alternative 1 with Ri3.

Figure 31: MCU Intermediate Coat standard with no rusting on the surface.

3.13. Accelerated weathering test: QUV-B

The test lasted 150 hours but during this period assessments were done at 24 and 100 hours.

- **Assessment 24 hours**

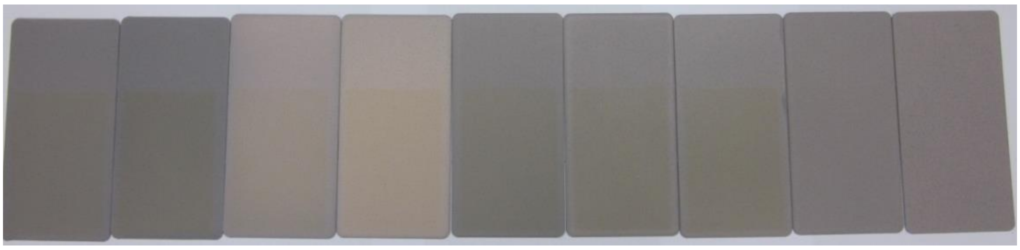


Figure 32: MCU Intermediate Coat QUV-B results after 24h. From left to right: MCU Intermediate Coat, alt1, alt2, alt2 extra, alt3, alt4, alt5, alt6, alt7.

There was yellowing in all the aromatic 1K PU panels whereas the aliphatic 1K PU had no change in colour at all.

Table 21: QUV-B results after 24 hours.

QUVB Panels	dE after 24 hours
MCU Primer	4.47
MCU Primer ALT 1	3.58
MCU Primer ALT 2	4.49
MCU Intermediate Coat	5.83
MCU Intermediate Coat ALT 1	7.31
MCU Intermediate Coat ALT 2	7.18
MCU Intermediate Coat ALT 2 extra	5.96
MCU Intermediate Coat ALT 3	5.96
MCU Intermediate Coat ALT 4	6.76
MCU Intermediate Coat ALT 5	6.80
MCU Intermediate Coat ALT 6	0.47
MCU Intermediate Coat ALT 7	0.28

All the panels have failed already after 24 hours due to the aromatic resin. Just alternative 6 and 7 have acceptable colour difference.

We skip the images from 100 hours assessment due to the fact that only two panels were acceptable and we show the final assessment.

- **Final assessment 150 hours**

Table 22: QUVB final assessment.

QUVB Panels	dE after 150 hours
MCU Primer	4.00

MCU Primer ALT 1	4.85
MCU Primer ALT 2	3.69
MCU Intermediate Coat	3.50
MCU Intermediate Coat ALT 1	4.43
MCU Intermediate Coat ALT 2	4.60
MCU Intermediate Coat ALT 2 extra	5.98
MCU Intermediate Coat ALT 3	5.67
MCU Intermediate Coat ALT 4	5.2
MCU Intermediate Coat ALT 5	5.95
MCU Intermediate Coat ALT 6	0.88
MCU Intermediate Coat ALT 7	0.40

The values after 24 hours are the most significant because the aromatic paints were already decoloured. The values after 100 and 150 hours may decrease or increase but is not representative, the paint is already failed. The only values which are representative after 100 hours and 150 hours are the ones of MCU Intermediate Coat alt6 and alt7.

As topcoat MCU Intermediate Coat alt 7 is the best resisting weather conditions as figure 33 shows.

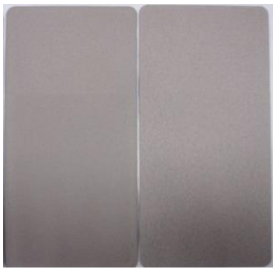


Figure 33: Alternative 6 on the left and 7 on the right after 150 hours QUV-B exposed.

3.14. Results overview

We have already seen all the results obtained with the alternative formulas proposed to the standard MCU formulas of Hempel. In this section we will show the summary tables of the results.

- **MCU Primer results overview**

Product	Alternative	Results									
		Price	Sagging	Drying time (h)	Stability (1 month)	Final fim hardness (König)	Flexibility (mm)	Adhesion (cross-cut)	Impact (mm)	SST 240 h	QUVB 150h
MCU Primer	Standard	STD	60	2	Ok	35	6	0	>20	Ri2	High
	1	STD + 1,7%	30	1	Ok	45	8	0	>20	Ri1	High
	2	STD +20%	25	2	Ok	45	5	0	10	Ri0	High

Table 23: MCU primer results summary.

Both alternatives show better performance than the standard but alternative 2 gave the best results:

- Without MDI based isocyanate resin (alt1) the results are quite similar to standard.
- Without MDI resin and MDI water scavenger (alt 2) all the parameters except sagging are improved. The best alternative: MCU Primer Alternative 2.

MCU Primer alternative 2 only visible defect is the higher price. This alternative uses MDI free resins, instead of E152 from standard it uses E155 and as water scavenger D755 is deleted. So we can conclude that for 1K PU primers E155 as main resin and E156 as flexibilizer is good mix of resins. On the other hand, D508 and D509 are also a good combination of water scavengers for 1K PU primers.

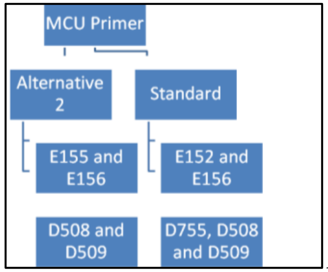


Figure 34: MCU Primer best formula compared with standard.

- **MCU Intermediate Coat results overview**

Table 24: MCU Intermediate Coat summary.

Product	Alternative	Results										
		Price (eur/ Kg)	Sagging	Drying time (h)	Stability (1 month)	Final fim hardness (König)	Flexibility (mm)	Adhesion (cross-cut)	Impact (mm)	Abrasion (mg lost)	SST 120h	QUV B 150h
MCU Intermediate Coat	**Standard**	STD	25	0.5 (4h max)	Difficult to apply	50	>13	5	15	34	Ri0	3.50
	1	STD -4%	35	3.5	Difficult to apply	30	6	0	12.5	43	Ri3	4.43
	2	STD +7%	10	0.5	Difficult to apply	50	>13	5	12.5	13	Ri0	4.60
	2 extra	STD + 11%	20	8	Low Sagging	15	<5	5	20	11	Ri0	5.98
	3	STD + 14%	20	1	Difficult to apply	80	>13	5	10	22	Ri0	5.67
	4	STD + 29%	20	3.5	Ok	45	5	0	10	19	Ri0	5.2
	5	STD + 36%	30	3	Ok	50	6	0	12.5	21	Ri0	5.95
	6	-	60	11	Low Sagging	20	8	2	20	77	Ri3	0.88
	7	-	60	11	Ok	45	8	5	10	46	Ri4	0.40

In MCU Intermediate Coat there are two critical parameters that let us choose the best alternative:

1. Stability: Alternatives 4, 5 and 7 are the only ones without application problems after 1 month of storage or sagging under specification. The most important fact to remember is that the alternatives with the best stability contain D509 which is water scavenger made exclusively for storage.
2. Drying time: Alternative 7 has more than 8 hours to dry so it cannot be used.

Therefore alternative 4 and 5 are the candidates for best MCU intermediate Coat formula despite the higher price.

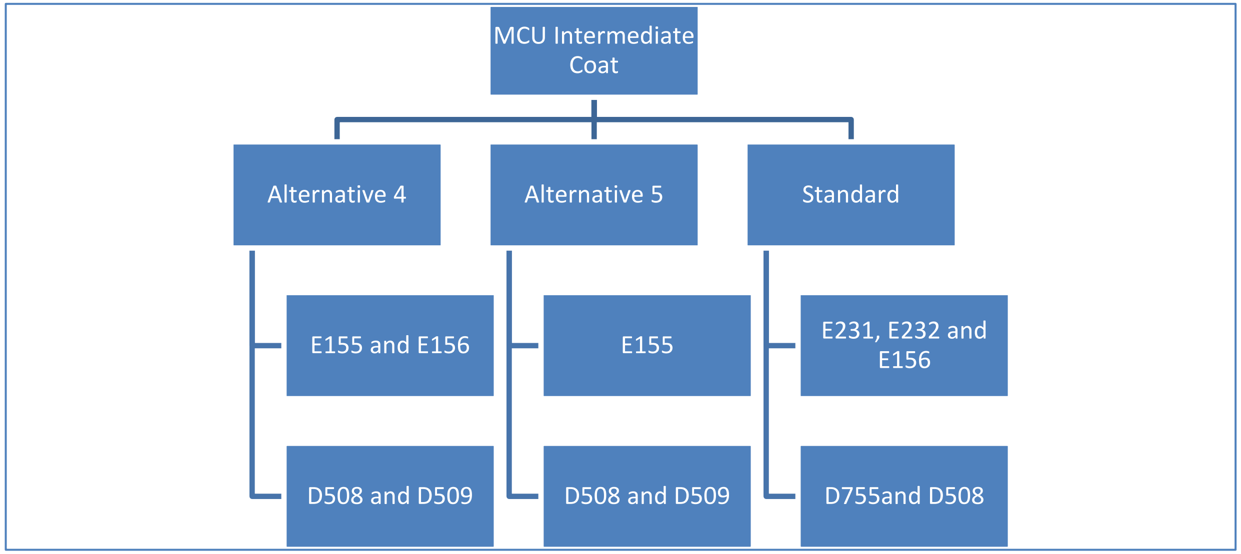


Figure 35: MCU Intermediate Coat best formulas compared with standard.

Both alternatives gave very good and similar results in all the tests for Intermediate Coat (QUVB would not be included for an intermediate coat). However we needed to decide which one should be the next formula for MCU Intermediate Coat, then finally Alternative 4 was decided.

The selection of Alternative 4 is given by the reduction of price compared to Alternative 5. Alternative 5 increases the price of the formula 36% whereas Alternative 4 increases the price 29% which is a significant difference for no properties profit. In addition alternative 4 uses the same resin system than MCU primer Alternative 2 therefore these resins can be storage in higher amounts which is more profitable for the company.

4. Conclusions

The study concluded successfully providing Hempel two new formulas without MDI isocyanates and improved properties. However along this study many findings were obtained.

First of all E155 with E156 (TDI based isocyanate prepolymers) shown very good performance, better than standard resins mixture of both 1K PU products. Therefore TDI prepolymers provide adhesion, flexibility, abrasion resistance, film hardness, stability and the rest of properties checked in this study in higher level than MDI based prepolymers. Their only negative point is the higher price.

Then we found out that D508 is very good alternative to D755 as coating manufacture process water scavenger. Para Toluene Sulphonyl Isocyanate gave the same or even better high reactivity with moisture than MDI water scavenger.

The clearest finding for 1K PU future formulations was triethyl orthoformiate (D509) which was essential for storage stability of these coatings.

Finally we could say that aliphatic isocyanate resins are the most indicated for topcoat applications but they need accelerators to have acceptable drying times.

Regarding the rationalisation of Hempel raw materials out of 8 raw materials necessary to have in stock for 1K PU Hempel products we can reduce this assortment significantly.

The original raw materials were:

- Resins: E152, E155, E156, E231, E232
- Water scavengers: D508, D755, D509.

It is possible to have the same products quality and even better being out of R40 labelling with 4 raw materials in assortment:

- Resin: E155 and E156
- Water scavengers: D508, D509.

E155 has been chosen as main resin for 1K PU in Hempel because in all the areas seem to have superior properties to the rest of resins without high health and safety risks. There are several reasons why E155 improves the performance of E152, E231 and E232:

- Provides flexibility due to the medium NCO %
- At the same time there is hardness and fast drying due to 61% SWR and 6.8% NCO, so when it is dry the %NCO effective of the resins is higher: 11.1% NCO.
- TDI based isocyanates provide more flexible films than MDI based polyurethanes as shown in this table imported from a scientific article [3].

Sample code	Mol ratio DDI[a]/Polyol	Volume ratio DDI[a]/Polyol	Modulus (MPa)	Ultimate tensile strength (MPa)	Ultimate elongation (%)
	TDI/PPEG	TDI/PPEG			
TPU2.5T	2.5	0.1	0.4	2.7	437
TPU5T	5	0.2	4.2	10.0	177
TPU10T	10	0.5	7.6	29.4	295
TPU25T	25	1	9.4	26.0	266
TPU50T	50	2	9.9	38.5	272
	MDI/PPEG	MDI/PPEG			
MPU10M	10	0.70	34.5	20.0	21
MPU5M	5	0.35	21.5	5.6	35
MPU3M	3	0.21	10.5	3.0	21
MPU1.5M	1.5	0.10	3.4	0.9	25

Figure 36: TDI versus MDI polyurethanes.

TPU means thermoplastic polyurethane, 5T/M and 10T/M means molar ratio: TDI or MDI versus polyol. For TDI batches the ultimate elongation is higher than MDI, thus TDI films are more flexible.

Annex

1. Introduction to 1K PU theory

1.1. Moisture cure polyurethane coatings theory basis

Moisture cure polyurethane coatings are urethane coatings classified as type II **(**or type IV if isocyanate is pre-polymerised and catalysed urethanes) by ASTM D-16 specification (fig 37). They are single package composition (one component curing coatings) therefore the main resin does not need another manufactured product to form a film.

Table 16-6
Major Categories of Urethane Coatings

Category	Cure Mechanism	ASTMD — Classification	Applications
Oil Modified Urethanes	Oxidizing	Type 1	Trade Sales
Moisture Curing Urethanes	Reaction with Atmospheric Moisture	Type 2	Industrial Maintenance Flooring
Blocked Urethanes	Heat Initiated Reaction Between — OH and — NCO Species	Type 3	OEM and Automotive
Prepolymer plus Catalyst	Reaction with Atmospheric Moisture	Type 4	Flooring
Two Component Urethanes	Room Temperature Reaction Between — OH and — NCO Species	Type 5	Industrial Maintenance OEM and Automotive
Urethane Lacquers	Solvent Evaporation	Type 6	OEM
Aqueous Urethane Dispersions	Coalescence		OEM and Automotive Trade Sales
Urethane Polyols	(Reactive Intermediate)		Polyols for Urethane and Other Polymers
Acrylated Urethane Oligomers	Peroxide Initiated Radiation Cure		OEM

Figure 37: Major categories of urethane coatings. [4]

The main resin in moisture cure polyurethanes is a prepolymer of isocyanate. This resin cures by the reaction of residual isocyanate groups (usually 2-4.5 percent of the resin’s weight) with atmospheric moisture to form disubstituted urea and biuret-linked polymers. [4]

The reaction of these products with atmospheric water in the field involves a two-stage process with the water and the isocyanate groups first producing the unstable carbamic acid, which immediately dissociates to form an amine and carbon dioxide. The carbon dioxide leaves the film by evaporation, and the amine reacts with a second NCO group giving a urea (Fig.38).

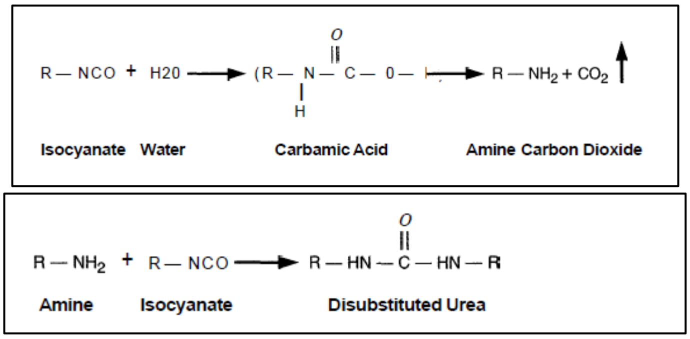
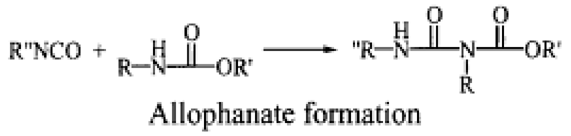


Figure 38: Isocyanate sequential reaction with moisture

Isocyanate moiety is very reactive therefore is very easy to have secondary reactions in the coating. (Table 25)

Table 25: Isocyanates main reactions

Hydrogen Donor Class	Isocyanate	Reaction Product
Water		Amine + CO2 leading to Urea
Hydroxyl groups		Urethane
Amine group		Urea
Urea		Urea Biuret
Urethane		Allophonate 
Carboxylic Acid		Amide

1.2. Parameters which influence 1K PU performance

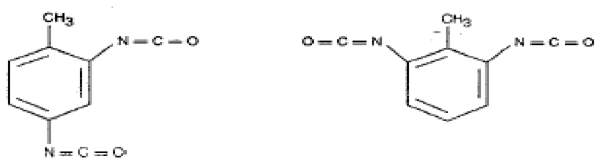
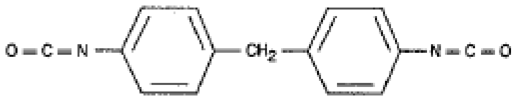
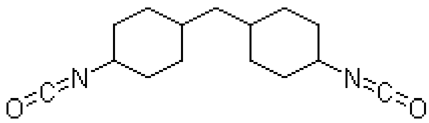
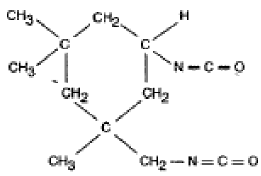
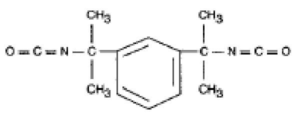
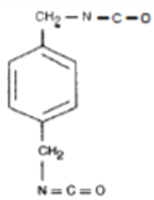
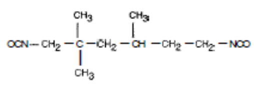
1.2.1. The resin

1K PU properties depends basically on the resin chemical composition which is isocyanate prepolymer composition.

1.2.1.1. Prepolymers formation and composition

In order to understand isocyanate prepolymers formulation it is very important to know the chemical composition of isocyanate monomers. In table 26 there are the most common isocyanate types.

Table 26: Most common isocyanate monomers

Abreviation	Chemical name	Chemical Structure
TDI	Toluene diisocyanate	
MDI	Diphenylmethane diisocyanate	
HDI	Hexamethylene diisocyanate	
H12MDI	4-Dicyclohexymethane diisocyanate	
IPDI	Isophorone diisocyanate	
TMXDI	P-Tetramethylxylene diisocyanate	
XDI	Xylylene diisocyanate	
TMHDI	Trimethyl-hexamethylenediisocyante	

Linear isocyanate monomers provide slower curing and do not have the solvent resistance and hardness because mostly they have low NCO content.

However there are self reactions involving the reaction of two or more isocyanate groups to produce dimers and isocyanurates (3 isocyanates) mainly. There are other reactions to form products like carbodiimides but as they are not used in this project we do not enter in this matter.

Dimerization forms uretidiones. This reaction is exothermic and can be done without catalyst or with catalyst like phosphines or pyridine. (Fig. 39)

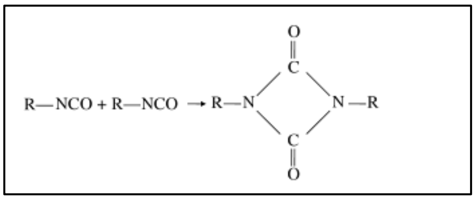


Figure 39: Dimerization of isocyanates

MDI for example, dimerizes at room temperature even though in the solid state.

Heating isocyanates leads to trimerization with the formation of very stable cyclic isocyanurates (fig.40). The rate of reaction is markedly increased by using basic catalysts.

This isocyanurate allow the introduction of chain branching and crosslinking. The thermal stability of the isocyanurate ring can offer fire resistance. [5]

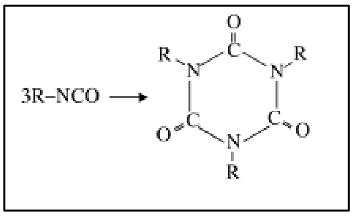


Figure 40: Trimerization of isocyanates

When isocyanurates are highly crosslinked they provide higher hardness, solvent resistance and faster curing. Therefore, branched and high NCO content isocyanate monomers will provide the best performance.

Nevertheless most isocyanates homopolymerize giving an isocyanurate structure, thus some branching and higher NCO is already obtained.

In the next figures we can see the homopolimerization of the most common isocyanates in the market.

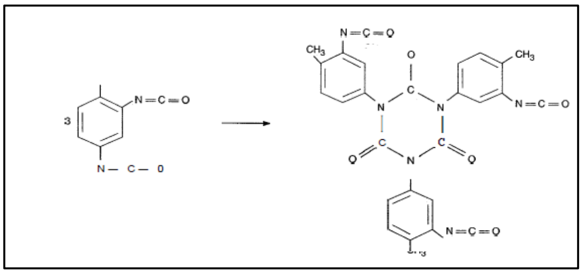


Figure 41: TDI trimerize giving stable isocyanurate ring structure.

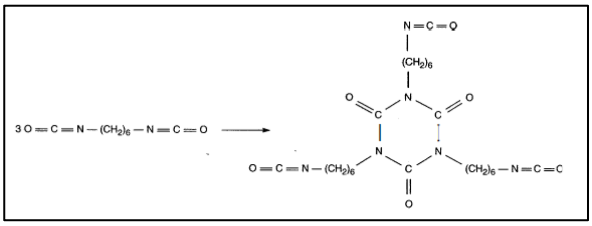


Figure 42: HDI trimerize giving stable isocyanurate HDI.

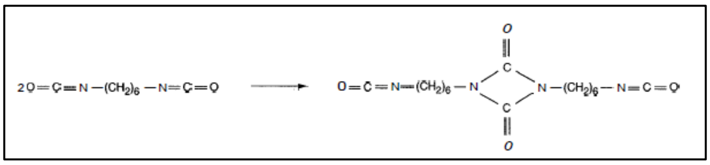


Figure 43: HDI also dimerizes giving HDI uretdione which is less stable and since 2010 restricted its application to non spray use by GHS (Globally harmonized system).

There is another type of isocyanate prepolymers which consist on pre-reacted isocyanates with hydrogen donor, they are called isocyanates adducts. The isocyanate adduction is mostly formed by excess of isocyanate which reacts with hydrogen donor substance (polyester, polyether, polycaprolactone or polycaprolactone). The result of this reaction is a prepolymer with functionality of two or more giving an isocyanate-terminated product that can be subsequently used for highly crosslinking with water.

1.2.1.2. Chemical composition and performance

High molecular weight pre-polymers are less sensistive and dependent upon humidity for final cure. They are usually applied on bridges and other immersed pieces.

Aromatic prepolymers are recommended for high film thickness coatings due to the ease to evacuate CO_2 and faster curing because of their high reactivity. Their low carbon dioxide generation and no skin formation on the surface allow the film to reach high film thicknesses.

They are used also for high PVC coatings so the principal use of them is as Zn rich primers under epoxy, polyurethane or moisture cure urethanes and as intermediate coats.

Aliphatic prepolymers cannot reach the film thicknesses of aromatic without bubbling but faster drying can be achieved by catalysers like oxazolidine.

TMXDI based prepolymers are the most stable aliphatic adducts and provide excellent properties comparable to two package polyurethanes including light stability property. They have higher price and slower drying time because of that they require catalysts. TMXDI contains aromatic rings but they are not closely attached to isocyanate moiety, therefore this compound is considered as aliphatic.(fig. 44) The reaction of this compound is faster than other aliphatic isocyanate resins because steric interactions. [4]

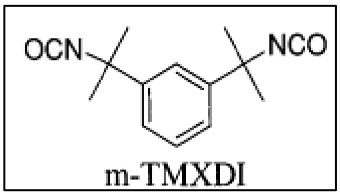


Figure 44: m-TMXDI structure.

1.2.2. The atmospheric moisture

Above 75 percent relative humidity, cure may be too fast and result in films bubbling as the carbon dioxide generated by the reaction is trapped in the set-up film. Below 30 percent humidity the coating cures too slowly, although the addition of tertiary amines or metallic catalysts speeds curing up. Figure 9 shows the limits of curing for these coatings depending on moisture.

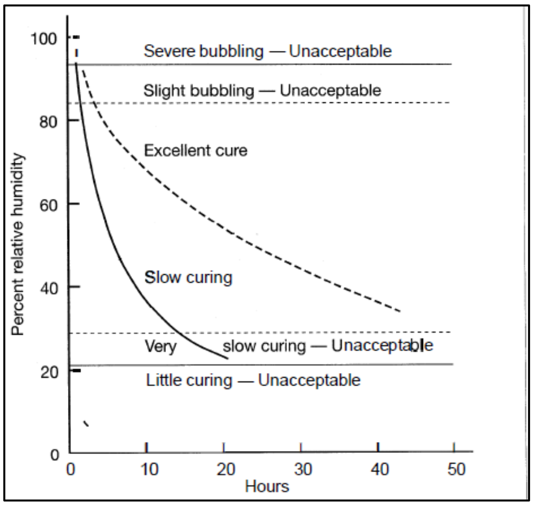


Figure 45: Effect of curing depending on atmospheric moisture.[4]

1.2.3. Film thickness

Bubbling becomes a more severe problem as film thicknesses increase because all the carbon dioxide generated in polyurea formation cannot be evacuated. High film thicknesses may also entrap solvent, especially where high boiling solvents are employed.

1.2.4. The pigmentation

The moisture present in pigmentation can vary significantly the stability of the moisture cure polyurethane. An amount as little as 0.5 percent of moisture in formula pigment causes a polyurethane of this type to gel in sixteen hours. Several routes around this problem have been considered. Some manufacturers roast their pigments to 110 ºC, slightly above the temperature at which water boils, before incorporation, although this methodology is not successful and some pigments may break down and change colour at high temperatures. Nevertheless the most used method is the moisture cure polyurethane manufacture under vacuum conditions and the addition of additives called water scavengers which absorb the water in the wet paint.

When flat plate pigments such as aluminium are used the moisture access to lower levels of film is delayed and bubbling problems may increase. The consecuence is a decrease on maximum film thickness threshold and then more than one layer coating must be applied.
Micaceous iron oxide is also a pigment commonly used either alone or in combination with aluminum as a barrier pigment in moisture curing polyurethane primers, intermediates, and finish coats. Compared to aluminium pigmented MCU micaceous iron oxide cure satisfactorily in very high humidity because their presence do not mean a decrease of moisture accessibility. As a matter of fact there have been done trials and coatings pigmented with micaceous iron oxide could cure in twenty minutes and be immersed.

1.2.5. Application temperature

Application temperatures have less effect than humidity, film thickness or pigmentation.

1.2.6. Water scavengers

These additives are the most important ones in moisture cure polyurethanes because they are responsible for absorbing water in the polyurethane production and storage. They allow the paint to be stable during longer time.

In the past molecular sieves which are molecularly porous alumino silicates (zeolites) designed to selectively absorb water were used around. Nowadays however more effective water scavengers are used and we can split them in two categories: manufacture or storage water scavengers. Highly reactive isocyanates such as monofunctional isocyanate toluene sulphonyl isocyanate (pTSI) or MDI are employed during pigment incorporation and they would be classified as manufacture water scavengers. On the other hand ethyl orthoformate is used in let down part of production because its function will develop during storage phase.

1.2.7. Storage conditions

The storage of moisture cure polyurethanes should avoid moisture to assure coating stability. The most used method to keep the wet paint without reacting is filling the can with inert gas, nitrogen gas.

Once the can is open the the coating must be used within a period of days or cure will advance to the point of gelation.

1.3. Advantages and disadvantages versus other systems

The principal advantages of moisture curing polyurethanes are:

1. They are single package paints and this means easier application and comfortability for the customer and production cost reduction.
2. Ability to be applied by brush, roller, trowel, squeegee, or spray without great demands on the applicator. This is because they have excellent flow and leveling, even when brush-applied and excellent aesthetics.
3. In wet areas the drying time is very fast and the painted piece can be immersed very rapidly. Moreover MCU are resistant to fungal and mildew growth.
4. The final films are typified by almost the same general property profiles that characterize all polyurethanes, great hardness without brittleness (even better than 2K PU), toughness combined with excellent elongation, and excellent resistance to acids, alkalis, halogens, sulphatea and other salts, solvents, and other strong chemicals. Light stability is, of course, dominated by the selection of the

isocyanate type, but aliphatic-based, specially TMXDI based moisture cure urethanes are recommended for exterior application.

5. For faster curing (specially in aliphatic based) tertiary amines, metal salt catalysts and alkanolamines which are usually employed in polyurethane coatings can be used.
6. When aliphatic based resins are used adhesion is excellent and even better than epoxies.

Unfortunately moisture cure polyurethanes show disadvantages in front of the rest of paints:

1. Moisture sensitivity and storage limitation.
2. UV resistance, flexibility and abrasion resistance cannot be as good as two pack polyurethanes due to urea linkages.

1.4. Areas of application

- According to ASTM-D standard classification II of urethane coatings: Moisture curing urethanes applications are industrial maintenance and floor coatings. When they are used with a catalyst they are class IV and they are used just for flooring. [4]
- Bridges and other immersed pieces like swimming pools due to fungal and mildew resistance.
- Highly corrosive environments
- Wood and concrete, particularly in interior
- Water and sewage treatment plants.
- Other maintenance applications for this type of material include ship interiors.

References

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[5] K.B. Tator, *Urethane coatings: Influence of chemical composition upon performance properties*, Journal of Protective Coatings & Linings, February 1985, p. 22.

Tables summary

Figures Summary