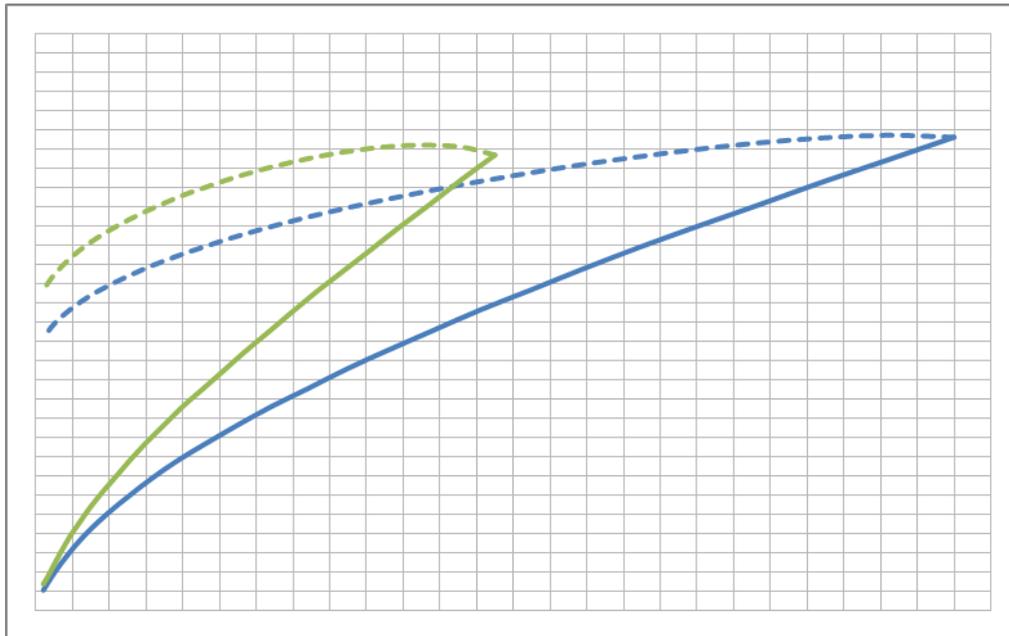


CHALMERS



Chemical Resistance of the Clear Coating of a Car An exploratory journey using Micro-Vickers hardness test with an emphasis on washer fluid

Bachelor of Science Thesis KBT X08

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Abstract

Testing the chemical resistance of a clear coating on a new automobile is time consuming and yields varying results depending on the procedures used. This report evaluates the existing standard regarding chemical resistance of the clear coating, with emphasis on washer fluid and attempts to investigate which variables have an effect on the recovery time of the clear coating after exposure. Hardness testing is introduced into the procedure and the importance of reaching the desired hardening level within the process is discussed.

The results give support to a new method, only using hindered evaporation. This can simplify the testing procedure and make it less time consuming. Temperature differences during testing proved to have a major impact on the chemical resistance of the clear coating. This results in recommendations for the use of different washer fluids during summer and winter and for different markets. Attempts to shorten the hardness recovery time indicated an ideal recovery temperature of 40 °C.

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1. Introduction

In the automobile industry the coating of a car is the main protection from external strains and interactions. Thus, it is crucial that the outmost layer of the coating, the clear coat, has adequate capabilities of resisting chemical and, to some extent, physical exposure. The aim of this report is to gain a greater understanding of the effects that washer fluids have on the clear coat and to develop a method that resembles the types of exposure that the clear coat of the car will endure during its life span.

There are several variables that may affect the interaction between the clear coat and the chemical that the lacquer is exposed to: Temperature, time of exposure, chemical properties of the external chemical and the type of clear coat that is used. This report intends to evaluate which variables and which properties in washer fluid have an impact on the clear coat and therefore are valid components to include in the final method.

The present method is evaluated with regard to swelling, discoloration, and adhesion. This project introduces hardness testing of the clear coat after exposure and compares the results with the hardness of the subject before testing.

1.1 Objective

This report intends to investigate the existing standard used at Volvo Car Corporation regarding chemical resistance testing of the clear coats with emphasis on washer fluid. The aim is to simplify and quantify the testing procedure, making it possible to produce reliable and consistent results.

2. Background

A variety of fluids comes in contact with and influences the clear coat of a car during its life span. Examples of these fluids are gasoline, coolant, battery acid, different types of oil and washer fluid. The latter is, by far, the fluid that the clear coat is most exposed to due to its frequent use to keep the windshield and headlights clean. Although the intent is to concentrate the washer fluid to the windshield and headlights, a substantial amount lands on the car paint.

A car is assembled from many different pieces and materials, thus, it is necessary for the protective coat of paint and clear coat to have different properties for different materials to provide the quality that is demanded.

The body of the car is based on a variety of steel and aluminum composites. The metal body is then cleaned and protected against corrosion in several “baths”. Phosphorylation and electro dipping are examples of this and they have an important role in the corrosion protection system of the coatings. After these pretreatment stages a first layer is sprayed on the body, called the primer. This layer enhances the corrosion protection but also increases the quality and smoothness of the finish. The second layer, the base coat, consists of the actual color intended for the car. The third and final layer is the clear coat and this layer is the cars first protection against external influences.

The type of clear coat used differs depending on which material it is applied to; on metallic surfaces the clear coat of choice hardens at approximately 140 °C whereas the clear coat applicable for plastic surfaces hardens at approximately 70-90 °C depending on the polymers glass transition temperatures of the plastic component.

When new types of clear coats are tested, one of the tests is the clear coats resistance to the influence of other chemicals. The current method for testing consists of placing a drop of fluid (the external chemical) on the clear coat. The test runs for two hours; one test with free evaporation and another with hindered evaporation. The hindered-evaporation test is done by placing a piece of filter paper on the clear coat and applying the drops onto the filter paper. Since evaporation still occurs in the hindered-evaporation test, the filter paper is refilled with drops of fluid every 15 minutes during the two hours of testing. The pieces of material tested are then washed with water and dish soap and then kept in a tempered room. After 24 hours, the test subjects are evaluated with regard to swelling, discoloration and adhesion.

A request from Volvo Car Corporation is that the new method should be reproducible, simple to use and produce reliable results that reflect the effects that washer fluid has on the clear

coating in reality. There is also a request to gain greater knowledge concerning how the hardness of the clear coat changes with varying exposure.

3. Theory

3.1 Coatings

The purpose of the coating of an automobile is to protect the mechanical properties of the underlying materials such as steel and plastic. If the coating is inadequate the steel will begin to corrode which can lead to fatal consequences.

There are several demands that a coating has to fulfill and as a customer, appearance is perhaps the most crucial factor. However, chemical, scratch and UV-resistance of a clear coat decides how the appearance of the coating will change over time.

The coating of a car is build up in several layers; the primer, the base coat and the clear coat. The primer is applied first and acts as corrosion protection, the base coat is the actual color of the car and the clear coat is the outmost layer giving the car its luster and its first protection against external influence.

The clear coat has to be hard enough in order to resist scratches, swelling, discoloration and adhesion as well as keeping its ductility to satisfy the flexibility that is required. It is also desirable that the clear coating has self-healing capabilities.

The clear coats basically composed of polymers that are hardened by heating the surface to a certain temperature and for sufficient time to achieve the desired amount of cross-linking between the polymers. Polyurethane, seen in figure 1, has superior capabilities of cross-linking and it meets the demands to resist scratches, swelling and discoloration.^[1]

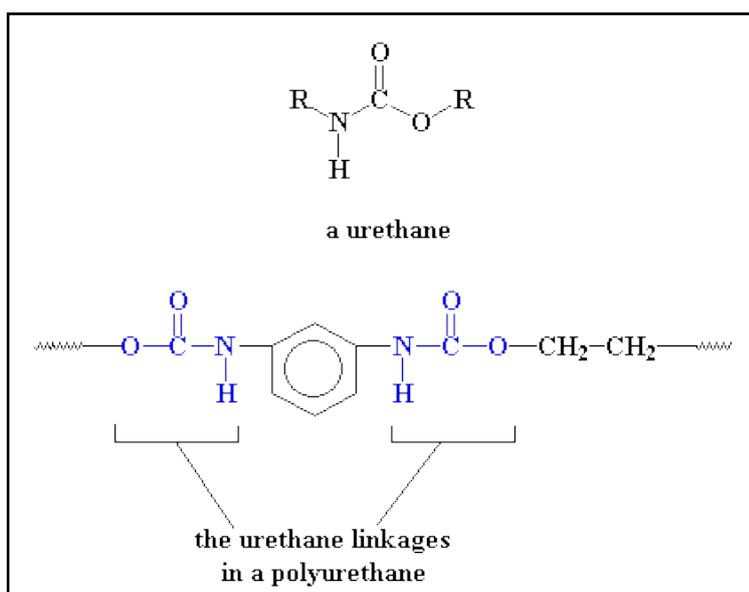


Figure 1 The structure of urethane and polyurethane. The upper molecule is the monomer urethane and the lower molecule is the polymer polyurethane.^[2]

The cross-linking or hardening of a clear coat depends on the hardening temperature, time, additives and the design of the specific polyurethane molecule. The clear coat becomes harder and displays increased self-healing capabilities with increased amount of silane-modified blocked isocyanate (SMBI) and it also performs better in scratch tests and chemical-resistance tests. ^[3] It is noteworthy that increasing the hardness of a clear coat makes it more brittle, thus losing some of its flexibility which can be undesirable depending on which component the clear coat is applied to.

The clear coat of a car is essentially a plastic without the typical additives such as softeners, fillers and stabilizers. This means that the clear coat displays similar mechanical properties as a plastic.

The response that the clear coat has to an applied pressure can be measured using the Micro Vickers hardness test, in which a diamond is applied to the surface of the sample with increasing pressure. The impression depth is measured continuously and compared with the current force. The program calculates the force over the impression depth, which results in hardness (N/mm^2). Figure 2 shows the elasticity of the clear coat and the difference of the start point to the end point represents the plasticity of the clear coat. It can be seen in figure 2 that the plasticity is not permanent; given time the impression depth goes back to its starting point.

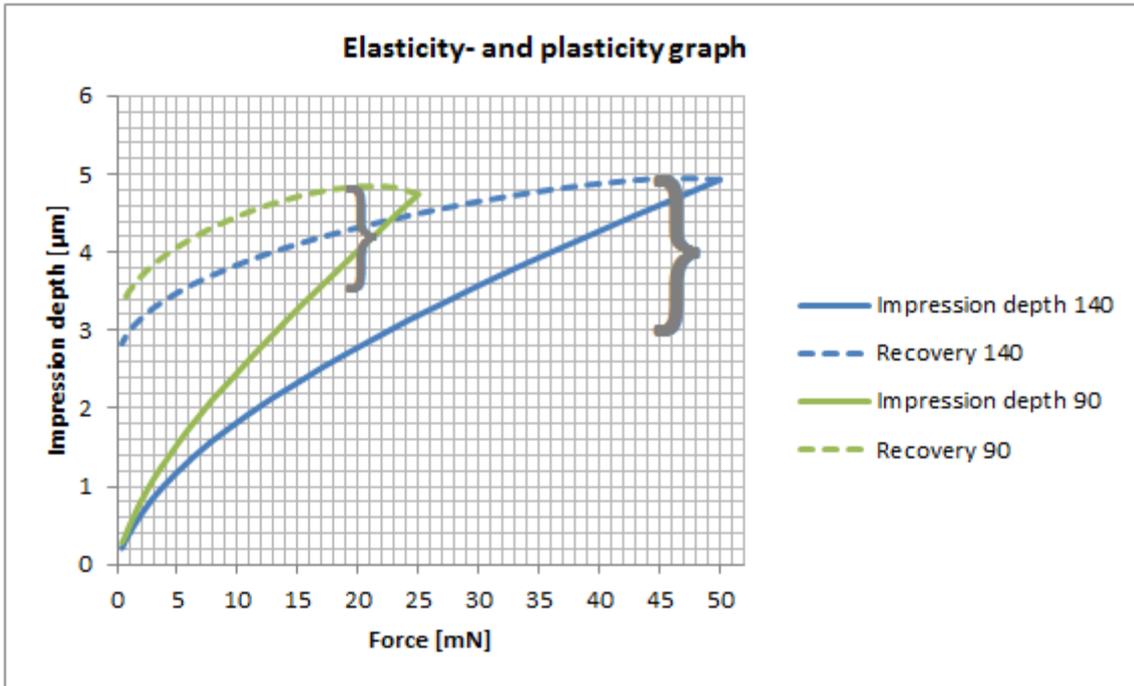


Figure 2 Correlation of force and impression depth using Micro Vickers hardness test. The solid lines represent the load-increase stage and the scattered line the load-decrease stage. The brackets indicate the elastic deformation and the difference of the starting point of the solid lines and the endpoint of the scattered lines are plastic deformation. 140 and 90 represent different clear coats, see table 1 for explanation.

3.2 Process

The standard temperature for hardening the clear coat that is applied on the body of the car is that the clear coat should reach 140 °C for 21 minutes. This is performed in three consecutive ovens. The first oven holds a temperature of 200 °C, and the only source of heat in the first oven is through heat radiation from the oven walls. The second oven holds a temperature of 170 °C and the third oven holds 140°C. The second and third ovens supply heat to the body through both heat radiation from the walls and convection by directed fans supplying the ovens with pre-heated air. ^[4]

The desired hardening level of the body is secured by controlling the parameters in the process and not by controlling the product. ^[4] The ovens are calibrated every time a new car model is released. However, the ovens use the same temperature levels and direction of heat-fan convection regardless of which model that passes. This means that there exists a compromise in cross-linking levels and thus the clear coats final hardness depending on which model that is tested and which part of the body. ^[4] Another parameter that has an effect on the hardening of the body is that the oven does not keep a constant temperature. The control system of the ovens is based on controlling the inlet of heated air to the ovens. The temperature of the inlet temperature in the first oven has a target temperature of 200 °C and can rise to 205 °C and sink to 145 °C. If the temperature rises above or sinks below those temperatures, an alarm is sounded to the maintenance team and they make the necessary adjustments. ^[4]

The allowed range in temperature of the heated inlet air to the ovens leaves a variation in the clear coat temperature and thus a variation in cross-linking. This results in a variation in the hardness of the clear coat, which in turn enables varying chemical resistance of the clear coat. To investigate this problem, this project used two under-hardened samples, 110 and 80. The 110 clear coating represents an under-hardened 140 clear coat and the 80 represents an under-hardened 90 clear coat. Table 1 describes the clear coats.

3.3 Washer fluid

The purpose of a washer fluid is to remove dirt, insects and pollutants from the windshield and headlights without having a negative impact on the materials of the car or the environment. Another important requirement is that the washer fluid has a low freezing point to ensure satisfactory capabilities in cold temperatures. Additionally, the use of a lubricant ensures that the windshield wiper maintain a continuous flow by lowering the friction between the windshield and the wipers. The lubricant also decreases the volatility of the washer fluid. This property ensures that most of the washer fluid is wiped away and not evaporated, which is important to prevent a thin whitish layer from building up on the windshield. ^[5]

Laws and regulation control the definition of a washer fluid, therefore the definition differs depending on the laws and regulations of different countries. In Sweden ethanol is defined as a washer fluid if it is denatured with 10 % isopropanol, 2 % methylene-ethylene-ketone and a color additive. ^[5] The additives do not have any cleansing properties; they merely make the ethanol undrinkable and thereby changing the classification of the product from alcohol to washer fluid.

The cleansing properties of a washer fluid are achieved by the addition of surfactants. There are four major types of surfactants: Anionic, cationic, non-ionic and amphoteric surfactants. The properties of these surfactants differ but their main purpose is to change the surface tension between the fluid and the surface. Amphoteric surfactants are prone to foam building, so they are not desirable for a washer fluid. Cationic surfactants act to form a protective layer. Some washer fluids containing cationic surfactants have been used, however most washer fluids contain primarily anionic and /or-, non-ionic surfactants.

In this project, three different washer fluids were used. Volvo's washer fluid, Lahega's washer fluid and the denatured ethanol used as base in Volvo's washer fluid. These fluids differ regarding which type of surfactants that are used. Volvo uses one anionic surfactant and one non-ionic surfactant whereas Lahega only has one anionic surfactant. ^[5] The denatured ethanol (DE), which does not contain surfactants acted as a blank during the tests. Volvo and Lahega also use different types of denature chemicals in the ethanol. ^[5]

The DE and Volvo's washer fluid were 100% when used as concentrate, whereas Lahega's washer fluid was 80% in concentrated form during this project.

The complete recipe for each washer fluid was made available to me for this project, however the recipes could not be written in this report due to company regulations.

4. Method and materials

4.1 Materials

To represent the clear coat of a car, a steel plate 10 x 20 cm was pre-treated in the same manner that the actual cars undergo. After the cleaning and pre-treatment stages, the primer was applied, followed by the paint; solid black is the standard because it reveals scratches, discoloration and swelling best. After the paint was applied, two different types of clear coats were used on different test pieces. The test pieces were then hardened in an oven at a certain temperature for a certain time depending on which type of clear coat that was desired. Table 1 describes the details for each clear coat and its area of use. Throughout this report, the different types of test pieces are referred to as 140, 110, 90 or 80.

Table 1 Different types of clear coats used in this project.

Test piece	Treatment
140	Hardened at 140 °C for 21 minutes, used for the body of the car, The Standard.
110	Hardened at 110 °C for 10 minutes, representing a failed hardening of the body.
90	Hardened at 90 °C for 45 minutes, used on plastic details, The Standard.
80	Hardened at 80 °C for 30 minutes, representing failed hardening on plastic details.

A constant-climate room was used for storage and evaluation during the project. The room was maintained at a temperature of 24 °C and a relative humidity of 50%. Each test had its samples stored and evaluated under these circumstances. Two of the tests, hardness recovery in 40 °C and 70 °C were stored in ovens at those temperatures and evaluated in the constant-room.

4.2 Test methods

Volvo Car Corporation requested that the method should be relatively simple and produce reliable and replicable results. The time of chemical exposure according to the existing standard, VCS 1026-81779, is two hours, and this standardized time was used throughout the project.

The first approach was to evaluate whether a difference between free and hindered evaporation existed. The hindered-evaporation test was performed by partially submerging a piece of painted metal (the samples) into a canister filled with concentrated washer fluid for two hours after which the sample was rinsed with tap water holding a temperature of approximately 10°C. This procedure was performed for three different washer fluids simultaneously: Volvo, Lahega, and DE. The samples were then evaluated with regard to swelling, discoloration, and hardness; the first two visually using Volvo Standard (VCS 1026-81779), and the latter using Micro Vickers hardness test, before the test, directly after being rinsed, and at one hour-, 24 hours-, 3 days-, 7 days-, 2 weeks-, and four weeks after the first evaluation. This timeline was used throughout the project and represents the x-axis for the graphs shown in Figures 4-9, see table 2.

Table 2 Timeline for the tests

Description	Time-line
Test 1	Before the test
Test 2	Directly after rinsing
Test 3	1 hour after test 2
Test 4	24 hours after test 2
Test 5	3 days after test 2
Test 6	7 days after test 2
Test 7	Two weeks after test 2
Test 8	Four week after test 2

The free-evaporation test consisted of continuous droplets applied to the test samples from burettes. A drop of concentrated washer fluid was applied to the sample, and the time of evaporation was measured. It takes just under 2.5 minutes for the concentrated washer fluid to evaporate, so the burettes were calibrated to release a drop of washer fluid every two and a

half minutes on-to the sample. The test lasted for two hours, and the evaluation process was repeated.

Both the free- and hindered-evaporation tests were performed on two different types of clear coat and each clear coat had two different hardening temperatures generating four samples for each trial, as shown in Table 1.

The second variable of interest was the dilution factor. The customer has two options regarding the purchase of washer fluid, they can either purchase a concentrated washer fluid or dilute it themselves or they can purchase a diluted “ready to use” product. The recommended dilution factor is 1:2, yielding a concentration of 33-volume%. The temperature that the car is expected to be exposed to is the basis for the dilution factor. When the concentration is increased the freezing point of the mixture is lowered. For example, a dilution factor of 1:2 yields a freezing point of approximately -18 °C whereas a dilution of 1:1 lowers the freezing point to -28 °C. [5]

For this study, a demarcation decided that the effects of dilution would be evaluated by comparing concentrated- and diluted washer fluid with a dilution factor of 1:2.

The tests were executed with hindered evaporation for 2 hours and the evaluation process was constant with every test.

The third variable investigated was the effects of temperature during the tests. Three temperatures were tested, -10 °C, 24 °C and 40 °C. Again, each test lasted for two hours, and the samples were submerged halfway, which represented hindered evaporation. [4] The tests were then rinsed and evaluated in the constant-climate room.

The samples were as mentioned earlier tested regarding hardness before the test, directly after and several times after that (Table 2). This yielded a “gap” in the graph from its initial hardness to its final hardness after the recovery stagnated. There was a request from Volvo that a test should be performed with a higher recovery temperature to investigate whether it could decrease the recovery time and thus decrease the time of evaluation. Two tests were performed at room temperature explicitly with Volvo’s washer fluid, both concentrated and diluted on the 140- and 90 clear coats. One of the tests recovered in an oven set at 40 °C and the other test recovered in an oven set at 70 °C. The tests were evaluated in the constant-climate room and then returned to the ovens between evaluations.

Swelling and discoloration evaluations were performed in accordance with the existing Volvo Standard for chemical resistance testing, VCS 1026-81779. Swelling and discoloration tests were performed on each sample that was tested during this project. Table 3 displays the grading level for swelling and table 4 displays the grading level regarding discoloration.

Adhesion testing was tested with the existing Volvo Standard, VCS 1029-54739. Since adhesion testing is destructive to the samples, the testing was performed on one batch. Table 5 displays the grading level for adhesion. There are several interesting alternatives concerning adhesion testing that enables a quantitative approach producing more replicable evaluations and thus increasing the reliability of the results.^{[3][6]} It should be stated that these tests require the sample to be a flat surface of a certain size. Therefore, they could only be used for tests on regulated test pieces and not on the actual shape and size of the component used in reality.

Table 3 Grading of swelling in the clear coat. ^[7]

Grade	Explanation
0	No visible swelling
1	Paint film somewhat swollen
2	Paint film clearly swollen
3	Paint film heavily swollen

Table 4 Grading of discoloration on the clear coat. ^{[7][8]}

Grade	Explanation
0	No discoloration of the paint film, grade 10 according to VCS 1026-51729, assessment scale B
1	Slight discoloration of the paint film, grade 7-9 according to VCS 1026-51729, assessment scale B
2	Clear discoloration of the paint film, grade 5-6 according to VCS 1026-51729, assessment scale B
3	Heavy discoloration of the paint film, grade ≤ 4 according to VCS 1026-51729, assessment scale B

Adhesion was tested in the following way. A grid was constructed with a scratch machine consisting of 25 squares, each 4 mm², in the clear coat. Tape was then applied on-to the grid area and removed quickly. The grid area was then examined with a loupe (three times magnified) and judged according to Figure 3.

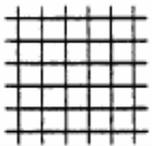
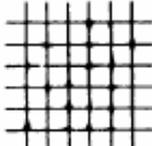
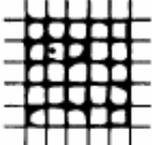
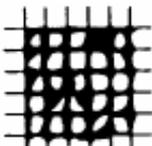
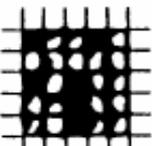
Grade Betyg	Evaluation Bedömning	Surface Yta
0	No remarks. The cuts are very sharp. No material has flaked. Utan anmärkning. Ritsarna är knivskarpa. Inget material är borta.	
1	Somewhat uneven cuts. Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area of max. 5 % may be affected. Något ojämna ritsar. I skärningspunkterna mellan ritsarna är mindre bitar borta. Frilagd yta får vara max 5 % av den totala ytan.	
2	Clearly uneven cuts. The coating has flaked along the edges and/or at the inter-sections of the cuts. A cross-cut area of max. 15 % may be affected. Tydligt ojämna ritsar. I skärningspunkterna mellan ritsarna är mindre bitar borta och/eller längs ritsarna är delar av rutorna borta. Frilagd yta får vara max 15 % av den totala ytan.	
3	Very uneven cuts. The coating has flaked along the edges of the cuts in large ribbons and/or some squares detached wholly. A cross-cut area of max. 35 % may be affected. Mycket ojämna ritsar. Längs ritsarna finns breda stråk av frilagda ytor och/eller om hela rutor är borta. Frilagd yta får vara max 35 % av den totala ytan.	
4	Severe flaking of material. The coating has flaked along the edges of the cuts in large ribbons and/or some squares have been detached partly or wholly. A cross-cut area of max. 65 % may be affected. Kraftigt bortfall av material. Längs ritsarna finns breda stråk av frilagda ytor, varjämte enstaka rutor är helt eller delvis borta. Frilagd yta får vara max 65 % av den totala ytan.	
5	A cross-cut area greater than 65 % is affected Mer än 65 % av den totala ytan är frilagd.	

Figure 3 Grading of adhesion in the clear coat. ^{[7][9]}

5. Results

5.1 Hardness

Figure 4 clearly shows that the free- and hindered-evaporation methods yield nearly the same results. The dashed lines represent free evaporation and the solid lines hindered.

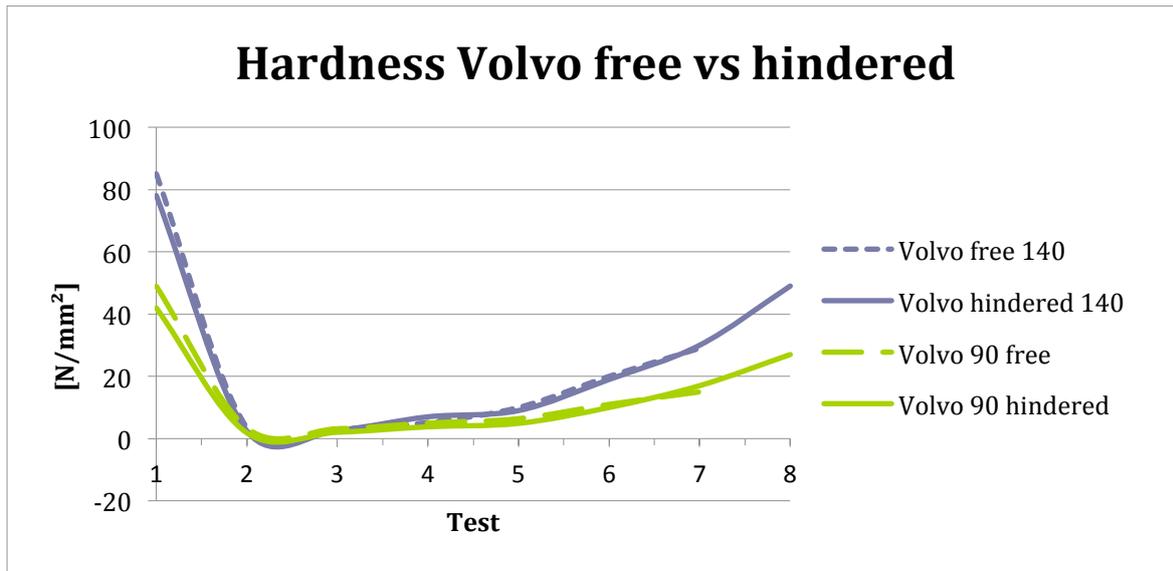


Figure 4 Hardness recovery, describing the difference between free- and hindered evaporation with two types of clear coats. 140 and 90 describes which clear coats that have been tested.

The experiment regarding dilution factor and its impact on the clear coat revealed that Lahega's washer fluid had the shortest hardness recovery time concerning concentrated washer fluid on both 140 and 90 clear coat. Volvo's washer fluid had the shortest hardness recovery time concerning diluted washer fluid on the 140 clear coats. However, Lahega's diluted washer fluid displayed slightly shorter hardness recovery time when used on the 90 clear coats.

The blank showed a slight increase in hardness with time for the 140 whereas it remained constant for the 90 test.

Figure 5 shows the difference regarding hardness recovery time between the three washer fluids. The samples were tested at room temperature and the figure describes the recovery time for the 140- and 90 clear coats. The results show that the diluted tests displayed shorter recovery times than the concentrated tests, however the differences were less for the 90 clear coat than the 140.

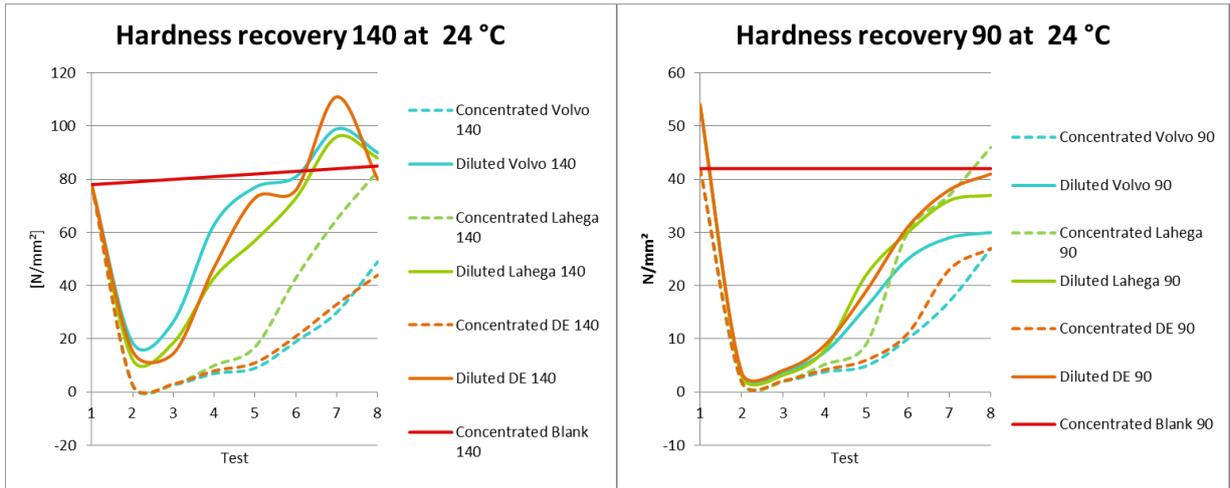


Figure 5 Difference in hardness recovery between concentrated and diluted washer fluids. To the left the 140 clear coats are tested and to the right the 90 clear coats. The solid red line describes the blank for each test. The scattered lines represent concentrated washer fluid samples and the solid lines represent diluted washer fluid samples.

Figures 6 and 7 reveal the impact that temperature has during the tests, and they show that there is a clear correlation between hardness recovery time and temperature during the tests. Figure 6 displays the hardness recovery for the 140 clear coats and it shows that the hardness recovery time increases with increased temperature; this is especially clear for the diluted samples.

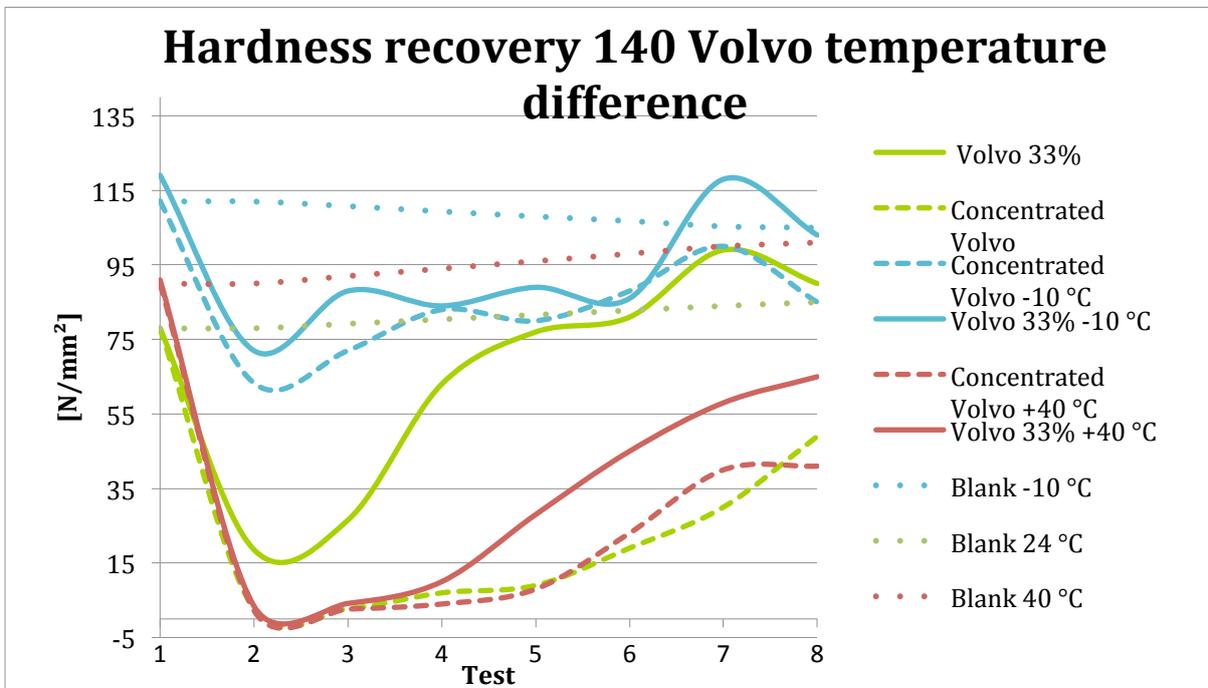


Figure 6 Impact that temperature has during the tests for the 140 clear coats partially submerged in Volvo's washer fluid.

Figure 7 indicates that the correlation between hardness recovery time and temperature is true for the 90 clear coats with diluted washer fluid samples as well. Such a correlation cannot be interpreted for the concentrated washer fluid samples for any of the clear coats.

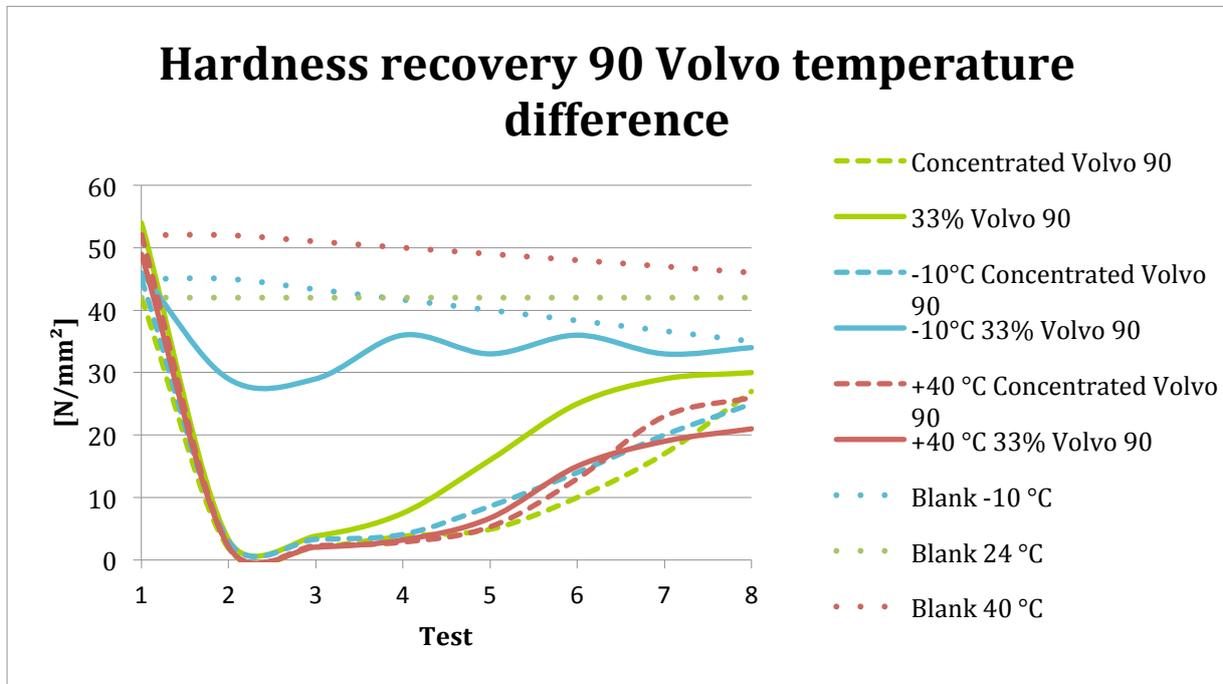


Figure 7 Impact that temperature has during the tests for the 90 clear coats partially submerged in Volvo’s washer fluid.

The tests regarding an increase in recovery temperature (Figures 8 and 9), clearly indicates that the hardness recovery time is shortened at higher temperature. This is true for both the concentrated and the diluted samples for the 140 clear coats. The blanks for the 40 °C and the 70 °C display a decrease in hardness over time.

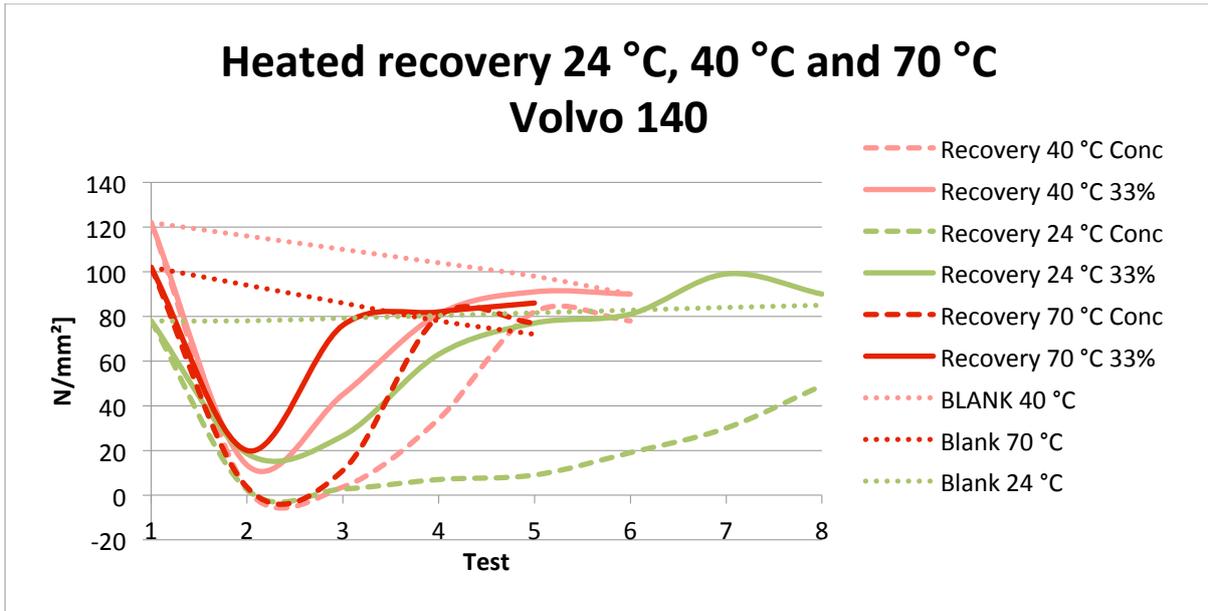


Figure 8 Difference of the "gap" which indicates that a decrease in hardness recovery time is correlated with an increase in recovery temperature for the 140 clear coats.

Figure 9 displays the same as figure 8 but it represents the results for the 90 clear coat. As well as for the 140 clear coats there exists a correlation between temperature increase and hardness recovery time decrease. This correlation is quite clear for both the concentrated washer fluid- and the diluted washer fluid samples in the 90 trial where each sample share similar results up to test 2, which was directly after rinsing, and differs substantially from test 3 and onwards.

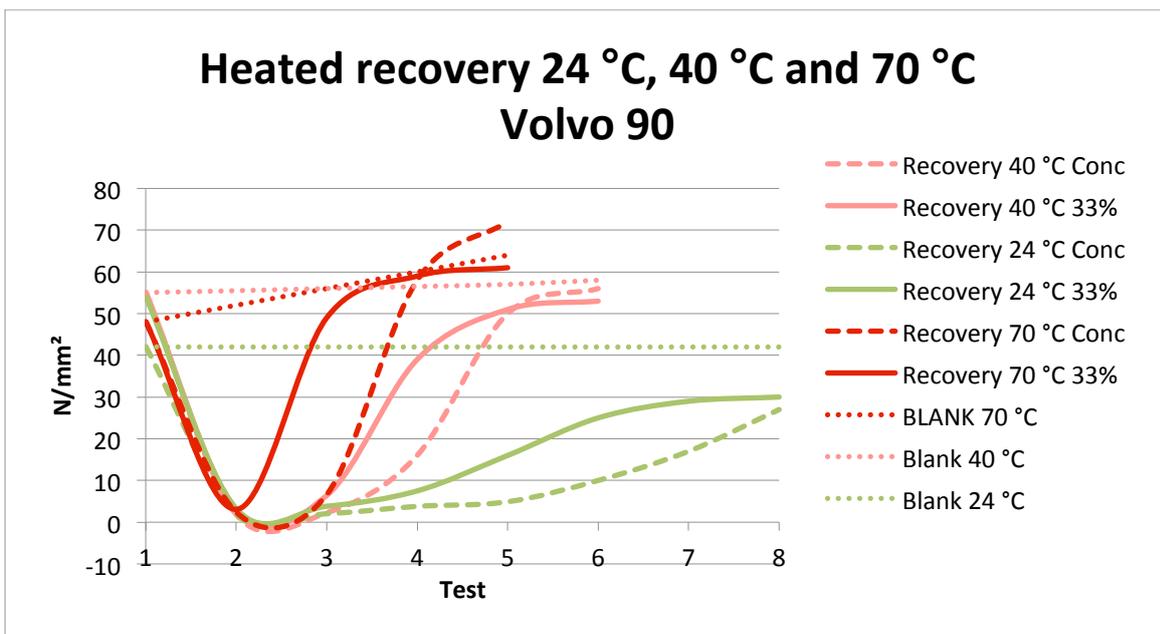


Figure 9 Difference of the "gap" which indicates that a decrease in hardness recovery time is correlated with an increase in recovery temperature for the 90 clear coats.

Quite different results were obtained in the diluted-sample tests. For these, the hardness recovery time, for the 24 °C sample 90, seemed to stagnate at 30 N/mm² at test 7 (2 weeks) and onwards, never reaching full recovery within the four-week testing period. When the temperature during recovery was increased to 40 °C the sample displayed almost full recovery at test 5 (3 days). When recovery took place at 70 °C the sample reached full recovery at test 3 (1 hour after rinsing).

The concentrated samples displayed similar results. The main difference was in the 140 trial where the concentrated sample reached 5 – 10 times lower hardness values in test 2 (directly after rinsing) than the diluted samples.

5.2 Swelling and Discoloration

Swelling occurred in every sample and a variation in recovery time was observed. The samples that were tested with concentrated washer fluid regardless of brand invoked a swelling between 1 and 2. This swelling followed the hardness recovery time and the swelling recovered fully for every sample that recovered fully or almost fully regarding hardness. The shortening of hardness recovery time, which an increase in temperature supplies, decreased the time of retraction regarding swelling. The samples that recovered fully regarding swelling received the grade 0. The samples that did not recover fully received a 1.

None of the samples during the project received any marks regarding discoloration and no turbidity was observed during the project in any of the samples.

5.3 Adhesion

Tables 6 and 7 display the results from the adhesion evaluations, in accordance with VCS 1029-54729. Table 6 responds to the concentrated washer fluid tests and table 7 responds to the diluted washer fluid tests. The testing of adhesion did not follow the hardness recovery time in any certain pattern. There was an obvious difference in the adhesion test depending on which clear coating that was tested. The standard coats, 140 and 90, performed better compared with the under-hardened coats, 110 and 80, on each trial.

Table 6. Results from adhesion tests of the four different clear coats tested with concentrated washer fluids.

conc	140			110			90			80		
Test	Volvo	L	DE									
1	0	0	0	0	0	0	0	0	0	1	0	1
2	0	0	0	2	1	0	0	0	0	0	2	0
3	0	0	0	2	1	1	1	1	3	2	3	2
4	0	0	0	1	0	0	1	0	1	1	2	1
5	0	0	0	0	0	1	1	0	1	2	1	1
6	0	0	0	0	0	0	1	0	1	2	1	1

Table 7. Results from adhesion tests of the four different clear coats tested with diluted washer fluids.

33%	140			110			90			80		
Test	Volvo	L	DE									
1	0	0	0	0	0	0	0	0	0	0	1	1
2	0	0	0	0	0	0	0	0	0	0	1	0
3	0	0	0	1	0	1	0	0	0	1	3	1
4	0	0	0	1	0	0	0	1	0	1	1	0
5	0	0	0	0	0	0	1	1	1	1	1	1
6	0	0	0	0	0	0	0	0	0	1	1	1

6. Discussion

The free- versus hindered-evaporation test was carried out using concentrated washer fluid. The results from these tests were interpreted such that the difference between free and hindered evaporation was small enough that hindered evaporation tests alone could describe the characteristics for both test methods throughout the project. This observation was an important step, making possible to evaluate further variables that might have been excluded otherwise.

The dilution factor test revealed that Lahega's washer fluid had by far the shortest hardness recovery time. This was not surprising considering that both Volvo and DE in concentrated form contains 100% washer fluid. Lahega's washer fluid used in this project contained 20% water yielding a concentrated washer fluid of 80%. This fact was known before the tests and taken into consideration when diluting the fluids to 33%. It is striking that such a small amount of dilution in Lahega's concentrated washer fluid had such a significant impact on the hardness recovery. The rather large impact that a small dilution has on hardness recovery time can be seen in appendix figure 1.

It would have been interesting to examine a 50% dilution to see if it would have given results in between the concentrated and the 33% dilution. Unfortunately, there was not enough time to carry out those tests in this project.

The impact that temperature had during the tests was very interesting. The inverse correlation between hardness recovery time and temperature during the tests was expected considering the physical properties of polyurethane and polymers in general.

However, the timespan of four weeks for this study was set and there was not time to evaluate the samples for longer periods. As can be seen in figure 5 and 6, some of the samples fully recovered within the four-week evaluation period. However, many of the samples did not and the trends of the lines suggest that the hardness had not stagnated. Thus, it would have been interesting to evaluate the tests in a greater timespan to see whether all of the samples would eventually recover fully or if a permanent impact on the hardness had occurred.

Testing the impact of an increase in temperature during the recovery period resulted in a shorter hardness recovery time for every sample in the trials. This correlation can be seen in figures 7 and 8 responding to 140 and 90 clear coats. The tests were performed exclusively for the 140 and 90 clear coats and only tested with Volvo's washer fluid, both concentrated and diluted. These limitations were decided because the 140 and 90 clear coats are the

standard clear coats and the decision of only testing them with Volvo's washer fluid was based on the time schedule.

The test regarding increased temperature during the recovery period was designed to investigate whether it was possible to shorten the evaluation time for the hardness tests. This seemed to work with both the 140 and the 90 clear coats. The 70 °C recovery temperature yielded the shortest hardness recovery time in both trials, however, it can be seen in figure 8 that the blank for 70 °C regarding the 90 clear coat increases in hardness over time. This might indicate that the temperature of 70 °C is too high, raising the temperature of the clear coat far enough above its glass transition temperature and thus enabling further cross-linking between the polymers. This can explain why the hardness increases during recovery in 70 °C but not in 40 or 24 °C. Further support for this explanation is that the blank for 70 °C in the 140 trial does not indicate an increase in hardness. Since the 140 clear coat has a higher glass transition temperature than the 90 clear coat it is expected that the hardness of the blank 70 °C for the 140 should remain constant or decrease. The hardness of the 140, before the test, was tested when the clear coat was 24 °C. Each test after that was made when the clear coat was 70 °C. Therefore, it is expected that the hardness of a clear coat should decrease with increasing temperature.

Swelling and discoloration was not the focus of this project and therefore only examined with the existing standards. Swelling occurred as described in the results and there was no discoloration found in any of the samples during the project. Unfortunately the swelling was not compared with hardness testing and thus no certain correlation between these parameters was established. Once the hardness of a sample recovered fully, a complete reversion of the swelling was observed. In hindsight it would have been desirable to examine this correlation further.

Adhesion was tested with the aid of a machine to ensure increased precision of the tests. It was difficult to specify the force needed because there existed a variation of sufficient force between the samples. This variation depended on which type of clear coat that was tested and at which time period it was tested. Another method for adhesion testing to ensure quantitative results would have been preferred in hindsight.

There was no certain correlation between swelling and adhesion or hardness and adhesion. It is important to state that there might exist a correlation between these parameters even if they were not found in this project. Perhaps a more extensive testing could reveal such a correlation.

Finally, it should be noted that there exist several interesting alternative methods for testing adhesion that which have emphasis on quantifying and reducing variation in adhesion testing.^{[3][6][10][11]} These may be very helpful and produce results with higher credibility. However, these procedures require standardized sample pieces and are therefore not a practical alternative when testing market samples.

7. Conclusion

The testing revealed that the hindered-evaporation test produced very similar results compared the free-evaporation test. This discovery enabled further testing to be conducted exclusively with hindered evaporation and that method was chosen because it is simpler and less time consuming to perform.

The finding that a small addition of water to the concentrated washer fluid shortened the hardness recovery time substantially supports a suggestion of diluting the concentrated washer fluid to 80 % instead of 100% as it is today.

There was a substantial difference in the effect that the washer fluid had on the clear coat depending on which temperature the samples were tested. The results indicate that cold temperature aids the clear coat to resist hardness reduction. This finding encourages producers to decrease the amount of ethanol in washer fluids aimed for markets with mild to warm weather. It might be useful for customers to use different washer fluids during the summer and winter.

Testing, with increased temperatures during recovery, revealed that increasing the temperature during recovery shortened the hardness recovery time. Increasing the temperature too much pushes the 80- and 90 clear coats far enough above their glass transition temperatures that further cross-linking occurs, making these results unreliable. This finding results in a recommendation of a recovery temperature of 40 °C, which retains full recovery within 1-3 days depending on the concentration of the sample.

This project used a fixed chemical exposure time of 2 hours. It would be interesting to evaluate the time variable and its effect on the hardness recovery time.

Adhesion testing revealed that a new method yielding more quantitative results is needed and future projects concerning this issue are recommended.

The results found in this report recommend the following specifications for a new standardized method:

- It is sufficient to test the clear coat with concentrated washer fluid. If the test fails with concentrated washer fluid, repeat the test with diluted (33%) washer fluid.
- The sample should be tested for hardness using the Micro Vickers hardness test before subjecting the sample to the washer fluid.
- The sample should be tested by partially submerging the sample in the washer fluid (50% submerged).
- The time of exposure should be 2 hours.
- The sample should be rinsed with cold water and carefully dried with paper.
- The sample should recover at 40°C for 72 hours. If the sample does not reach full recovery within 72 hours it fails the test (It is possible for the sample to recover at 24°C but it takes up to 4 weeks for the sample to reach full recovery. If the sample has not reached full recovery within 4 weeks it fails the test)
- The sample should be room tempered before hardness testing is performed, therefore the sample should be placed in the constant climate room 2 hour before evaluation.
- If the hardness value scores within +/- 20% of the original value it is regarded as full recovery.
- If the test fails the hardness test, adhesion test should be performed according to VCS 1029-54729.

Table 5 Suggestion of grading scale for hardness testing of the clear coat

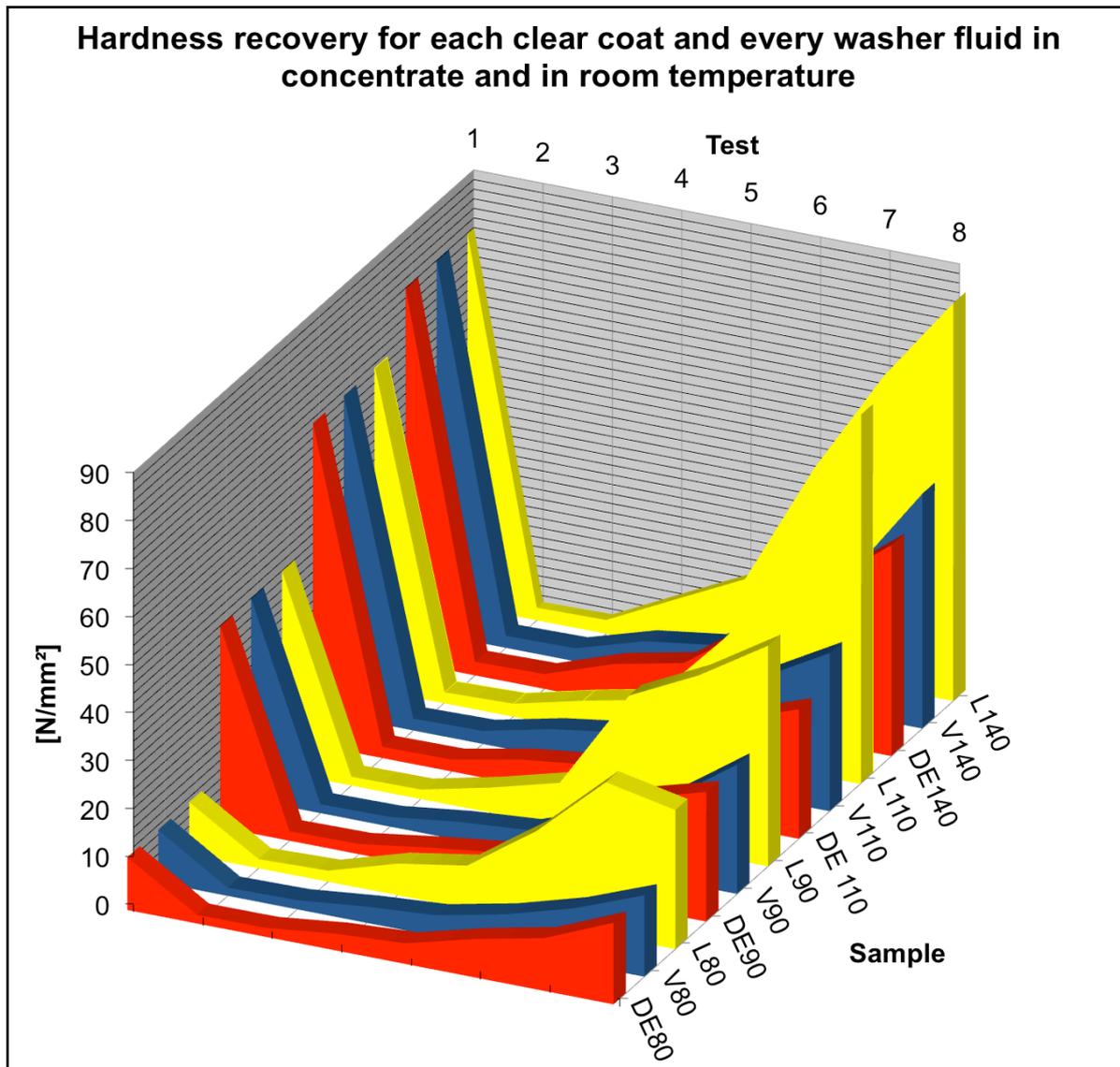
Grade	Description
0	Sample reaches full recovery. Within +/- 20% of the original value
1	Sample recovers 70-79% of the original value
2	Sample recovers 60-69% of the original value
3	Sample recovers less than 59% of its original value

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Appendix



Appendix Figure 1 Benefits of diluting a concentrated washer fluid from 100% to 80% regarding hardness recovery time. The red area indicates Denatured Ethanol (100%), the blue area indicates Volvo's washer fluid (100%) and the yellow area indicates Lahega's washer fluid (80%).