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Evaluation of Additives to improve the flow and leveling properties of OEM Top Coats

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ABSTRACT

This study shows that modified polyethersiloxanes and polyacrylates are important to optimize optical appearance of high gloss coatings. The effectiveness or possible adverse effects of the additives depend on their specific structure in the used paint system. Different modified polyethersiloxanes are presented with their characteristic behavior. Additives with various organic modification and with or without reactive groups are checked. The surface flow control agents are tested out in an OEM clear coat and a refinish 2 pack PU clear coat. The properties of the additives are checked at the applied coating. The results in gloss, haze, long wave, short wave, slip and intercoat adhesion are presented in this study. However, the „ state of the art“ for ideal flow and leveling is best obtained by using a combination of an acrylic and siloxane based surface control additive.

Diese Studie zeigt, dass modifizierte Polyethersiloxane und Polyacrylate eine wichtige Rolle spielen das optische Erscheinungsbild von hochglänzenden Lackierungen zu verbessern. Die Wirksamkeit und möglichen unerwünschten Nebeneffekte sind abhängig von der spezifischen Struktur der Additive und von dem verwendeten Lacksystem. Verschiedene modifizierte Polyethersiloxane und ihr charakteristisches Verhalten werden in diesem Artikel vorgestellt. Additive mit verschiedenen Modifikationen, mit oder ohne reaktive Gruppen, werden in dieser Studie überprüft. Die oberflächenaktiven Additive werden in einem 1 K Autoserienklarlack und in einem 2 K Reparaturklarlack getestet. Die Eigenschaften der Additive auf die Klarlacke werden am applizierten und vernetzten Film geprüft. Die Testergebnisse der Glanz-, Haze-, Long Wave-, Short Wave-, Haftung- und Slipmessungen werden in dieser Studie präsentiert. Optimale Ergebnisse im Verlauf und Leveling werden zur Zeit durch die Verwendung einer Kombination von acrylat- und silikonbasierenden Additiven erzielt.

INTRODUCTION

The automobile industry demands excellent surfaces. Paint manufacture steadily have to improve their coatings to match the demands of car producers. So additives improving flow and leveling are essential for developing new formulations with better appearance. To fulfil this task they are active at the surfaces coat/ air. The added additives do not have any impact on the technological properties. The adhesion or stonechip resistance for example has not to be influenced by additives.

The main tasks of Top Coats are good appearance and protection of the coated car. To accomplish this requirements the film must cover and spread over the complete surface of the car body. This seems to be a simple demand but usually it is more complicated.
After the paint has been applied, extremely complex physical and chemical processes take place during the drying processes of the coating film. Some of these phenomena are often simply called flow and leveling which are defined in the Paint and Coating Dictionary as follows:

Flow: Movement of a coating during and after application before the film has become solid. The movement depends on many factors for example rheological behavior of the paint or velocity of evaporation of solvents. The flow decreases with raising viscosity caused by evaporation of solvents. The rheological behavior is divided into five categories: newtonian, plastic, pseudoplastic, thixotrop and dilatant. After the application the shear rate is minimal and depending on the typical rheological behavior of the paint the viscosity of the applied paint increases. Theses causes a resistance to movement of a liquid paint. [1]

Leveling: The measure of the ability of the coating to flow out after application so that any surface irregularities such as brush marks, orange peel, peeks or craters, disappear during the drying process. These ability is achieved by a suitable surface tension. The better the leveling the smaller the surface tension gradient. Because of the evaporation of solvents gradients in surface tension may occur, so that the liquid flows to areas with high surface tension and that creates a lack of liquid in areas with low surface tension. A result of this effect is orange peel. [1]

CHEMISTRY OF FLOW CONTROL ADDITIVES

Polyacrylates and modified polysiloxanes are effective flow and leveling agents.

Polydimethylsiloxane have to be modified to be compatible with the paint. Unmodified polydimethylsiloxane are not compatible and cause negative side effects like craters. This were the experiences years ago. Today modifications of these polydimethylsiloxane are made for special demands. With the modification the compatibility with the paint system increases and no negative side effects origin. The compatibility is regulated by modification with polyether. The number of polyether side chains and the ratio of ethylene oxide to propylene oxides in polyethers achieve the solubility in the used system. The length of the polysiloxane chain regulates the typical behavior of the additive, for example if it is a leveling or a wetting control agent. The silicones are divided into dimethyl polysiloxanes, methyl phenyl polysiloxanes and organically modified polysiloxanes. So a special additive can be created for a certain task. Modified polysiloxanes can be built up with linear or comb structure and they can contain reactive groups.

Polyacrylates are divided in homo- and copolymers. Homopolymers have a regular and symmetric structure because they consist only of one monomertype. Copolymers can be built up with structures like AAABBB, ABABAB or ABBABA. With these structures the properties like compatibility of the additives are regulated. The compatibility influences gloss and haze. The polyacrylates are typical flow control agents without improving slip.

PROPERTIES

Surface control additives are able to minimize the negative influences to flow and leveling. Experimental work proves that there is a correlation between reducing the surface tension by surface control agents and the effectiveness of flow agents. Surface control additives orient themselves at the liquid/ air interface. This effect is

caused by a limited compatibility and the low surface tension of the surface control agents. With a lower regular surface tension the wetting, leveling and flow is improved. The wetting is improved because liquids only wet a substrate if their surface tension is lower than these of the substrate. The leveling is improved by creating a regular surface tension. Surface control agents orient themselves to the interfaces and so the evaporation of the solvents can not cause gradients of surface tension. Without these gradients there is no flow to areas with a higher surface tension and the orange peel does not occur.

This surface agents influence the coatings in many ways. All surface active agents should be checked carefully in the used paint system. Possible negative side effects can be: craters caused by overdose, interference in recoatability, foam stabilization, telegraphing or loss of intercoat adhesion. But after checking the additive carefully, many advantages can be provided by a surface active additive. This benefits can be: control of gloss and orange peel caused by a regular smooth surface. The control of substrate wetting is improved by reducing the surface tension of the wet paint. By reducing wet surface tension critical surfaces can be wet. A contaminant can not built up areas with different surface tension because the surface active additives equals the differences. Without these differences floating can be avoided. The slip is improved by reduction of surface roughness of the film which is influenced by flow and leveling. During drying the additives become concentrated at the surface. A closed film is formed, facilitating hydrodynamic lubrication when a solid body slides over the surface. In addition the anti- blocking effect is also improved. If the additive is soluble in the following applied paint the intercoat adhesion is not negatively influenced.

Wellknown organic polymers for solvent- borne coatings are acrylics, polyureas, melamines, cellulose acetobutyrates and polyvinybutyrals. Solvent- borne coating have generally low surface tension and in principle only modified polysiloxanes are surface- active in them.

TEST METHOD

The clearcoats were applied by an automatic spraygun. Gloss, haze, long wave, short wave, slip and intercoeat adhesion were investigated to determine the influence of the additives to the coating. High gloss coatings are measured at 20° angle and the reflected light intensity is compared with the emitted light intensity. Haze is caused by micro structures in the surface. The micro structure effects the direction of the reflected light. Haze is measured near the gloss angle. Long and short wave reflect the profile of the surface structure, but the differences in the profile are smaller than with orange peal. Long wave reflects structures bigger than 0,6 mm and short wave reflects structures smaller than 0,6 mm. The structures cause scattering in the direction of the reflected light. The force which is necessary to move a weight over the coating’s surface display the slip properties of the coating. The intercoat adhesion is checked by making crosscuts over the coating. With a tape the adhesion of the paint layers is checked.

The additives reduce the surface tension of the wet paint. So they improve wetting also. In the case that additives are soluble by the following paint layer the

recoatability is not being influenced. The additives act different in reducing the surface tension. This is shown in the figure below.

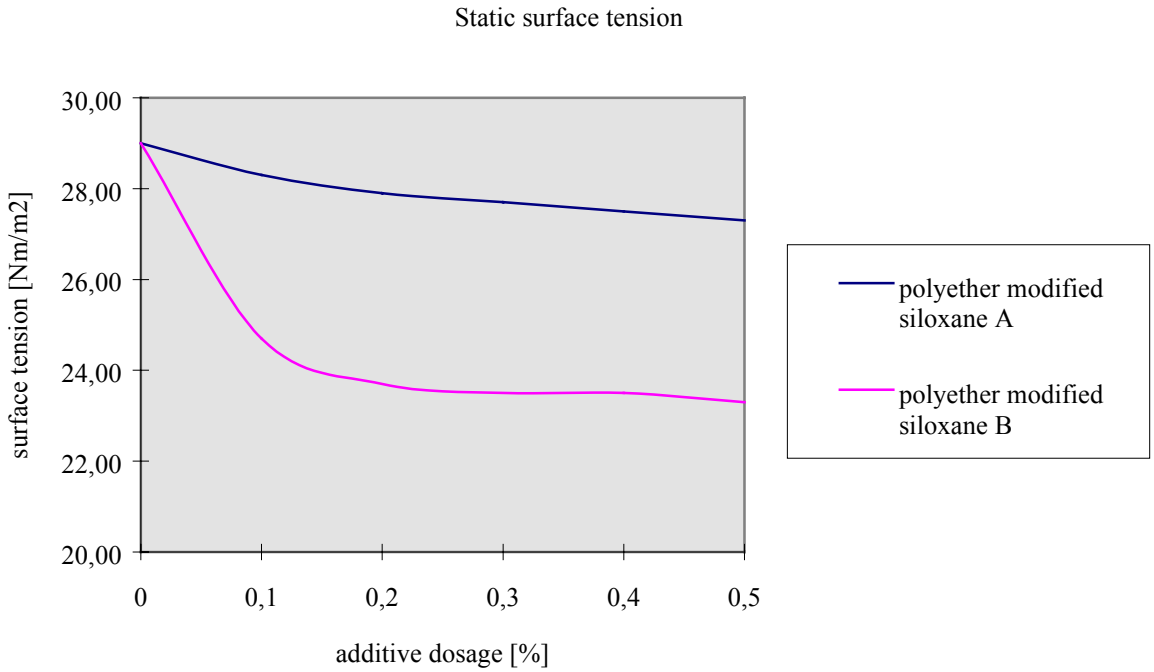

figure 1: reducing surface tension by adding additives with different structures

The leveling behavior depends on the dosage of surface control additives in the used system. Micelles are built by overdose and can change the previous positive results. Also the different types create different results in appearance. For example more polyacrylate is necessary to improve short wave than polyetehersiloxanes. The curves are totally different. Here it is checked in an OEM clear coat.

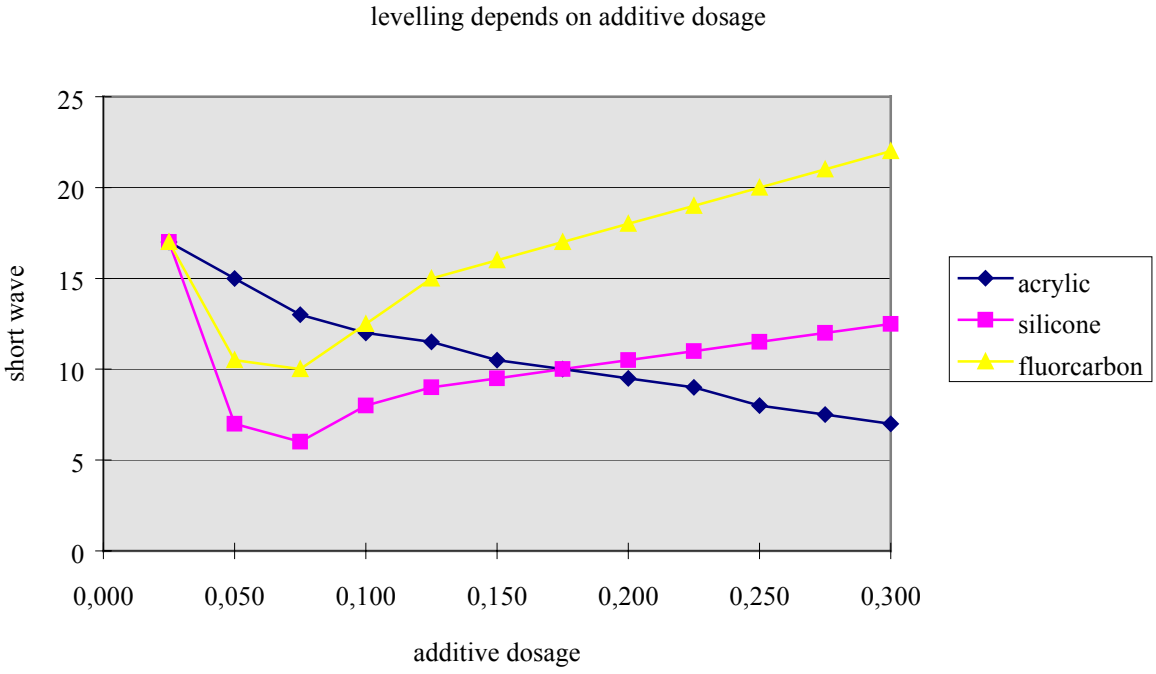

figure 2: different effectiveness of additives depending on dosage

In the following table the correlation between results of gloss, haze, long wave, short wave, slip and intercoat adhesion and the percent scale are shown.

gloss [20°]	haze	long wave	short wave	Slip [cN]	intercoat adhesion	Tego' s judgement
95 - 100 %	0 - 5	2 - 4	8 - 10	25 - 50	GT 0	**100%**
90 - 95 %	5 - 10	4 - 6	10 - 12	50 - 75	GT 1	**80%**
85 - 90 %	10 - 15	6 - 8	12 - 14	75 - 100	GT 2	**60%**
80 - 85 %	15 - 20	8 - 10	14 - 16	100 - 125	GT 3	**40%**
< 80 %	> 20	> 10	> 16	> 125	> GT 4	**20%**

Table 1: Judgement of test results

The results of adding different additives are shown by spider diagrams. With these diagrams variations of results can easily be shown. A complete filled spider diagram means that every task is fulfilled by 100 percent and the other way round. In praxis this is never reached, but an optimum should be reached. The results of the checked additives are shown in the following diagrams. The control without additives is shown in figure 5.

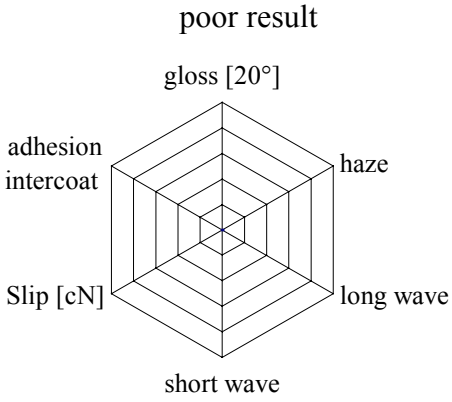

figure 3: poor result

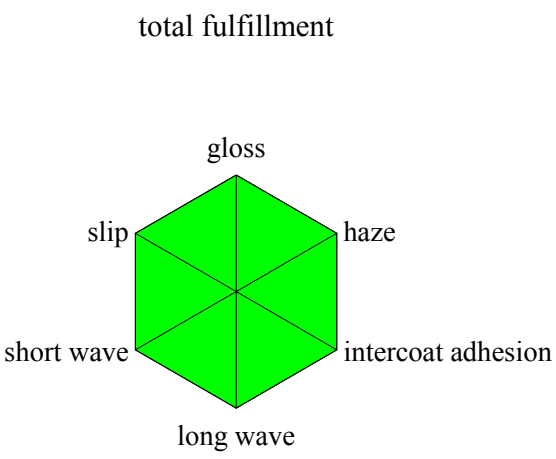

figure 4: total fulfillment

TESTED FORMULATIONS

In two different clear coat formulations surface active additives are checked and the results are presented as follows. The OEM clear coat is based on solvent- borne acrylic which is crosslinked with a melamine resin. The refinish clear coat is based on solvent- borne acrylic which is crosslinked with an aliphatic isocyanate. Usually surface control additives are added to the final paint. The addition level has to be optimized for each individual formulation. Different amounts should be considered to avoid undesirable side effects. The following results are presented by spider diagrams.

TEST RESULTS

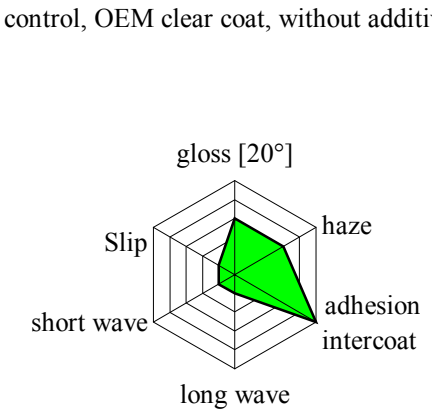

figure 5: results of the control, OEM clear coat

The gloss, haze, slip, short wave and long wave shall be improved. The adhesion is excellent but the appearance is not sufficient. In the first step 0,1 % acrylic homopolymer is added. The results are shown in the figure below.

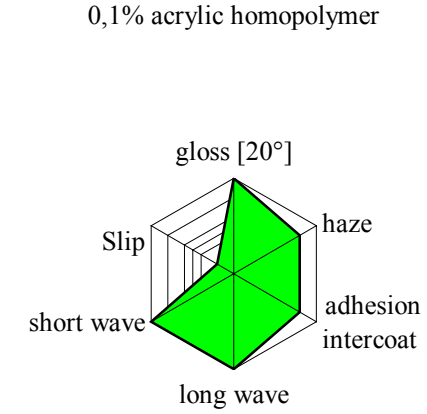

figure 6: results with added acrylic homopolymer additive to OEM clear coat

The next figure shows a different result to the homopolymer used before. A good result in haze indicates a good compatibility of the additive with the resins and solvents of the paint system. The different organic structure of the copolymer causes the limited incompatibility with the system. So a regular smooth surface is not built up. The intercoat adhesion is influenced if the additive is not soluble in the following paint layer.

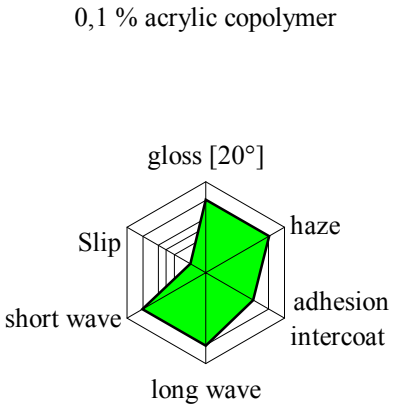

figure 7: results with added copolymer added to OEM clear coat

In the next figure the results of adding a silicone oil to the OEM clear coat are presented. Silicone oils are polydimethylsiloxane. The key property of the silicone backbone is the flexibility, rotation about bonds, the key property of the organic group is the surface activity. The chain is build like shown below. This silicone oils are the reason that paint formulator are afraid of craters by adding additives based on silicon. But today all additives are modified to avoid this negative side effects.

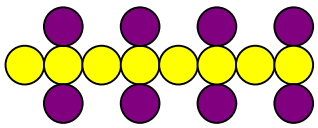

figure 8: scheme of silicone oils

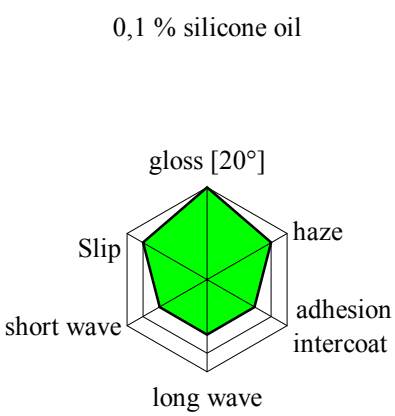

figure 9: results of adding 0,1 % silicone oil to OEM clear coat

The figure above shows the wellknown effect of silicone oils. The slip is clearly improved in comparison to the control but the silicone oils are not very compatible to the system. The long polysiloxane chain without organic modifications is not soluble in the system. The intercoat adhesion is poor because of the low surface tension so that the succeeding applied paint does not come to a direct contact with the substrate.

Polyether modified siloxane are build like shown below. The polyether improves the compatibility of the additive with the used clear coat system. Variations of polyethers achieve the solubility in the medium.The Si - O - C bond is not stable against hydrolysis, if the medium is acid and the additive is soluble in water. Under normal conditions no reaction is expected.

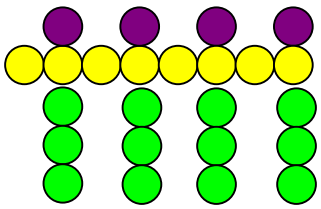

figure 10: scheme of polyether modified siloxane

The backbone orients themself towards the intercoation air/ paint and the polyether is oriented into the paint. The results of adding 0,1 % of a polyether modified siloxane, Si - O - C bonded are shown in the figure below.

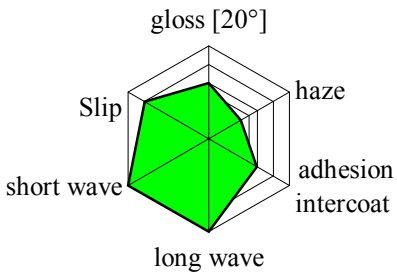

figure 11: results of adding 0,1 % polyether modified siloxane, Si - O - C bonded to OEM clear coat

The next additive is a polyether modified siloxane, Si - C bonded. This additives are stable against hydrolysis because they have no Si - O - C bonding. The structure is shown in the figure below.

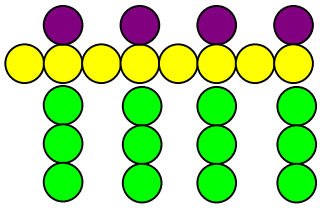

figure 12: scheme of polyether modified siloxane, Si - C bonded

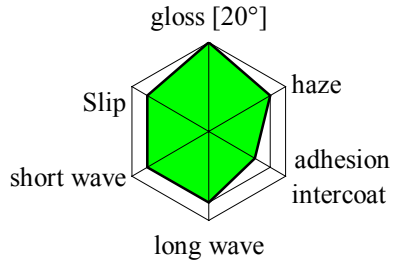

figure 13: results of adding 0,1 % polyether modified siloxane, Si – C bonded to OEM clear coat

In comparison of Si – O – C and Si – C bonding can clearly be shown that the Si – C bonding is more compatible to the system. In the diagram better results in haze and gloss are shown. But the Si – O – C bonded additive produces better results in leveling because of the limited compatibility. The methyl group is oriented to the

surface and creates a smooth surface. Every additive can be modified with several organic components to create special properties.

Another type of additive is a polyethermodified siloxane Si - C bonded surface control agent. It is hydroxy functional and the modification are placed in α and ω position.

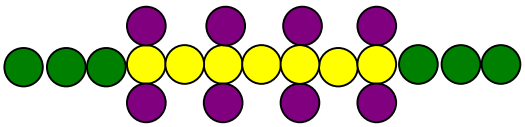

figure 14: scheme of polyether modified siloxane Si - C, hydroxy functional

This additive improves five of six targets but there is a loss of intercoat adhesion. If this additive does crosslink with the resins it causes insufficient intercoat adhesion. The results of these additive are shown below. If the additive reacts with the resins it is fixed at the surface and there the silicone backbone disturbs the wetting of the next paint. Because this type is fixed it can not be soluted by the following paint. For a good adhesion the additive on the surface must be soluble in this medium. The additive migrates.

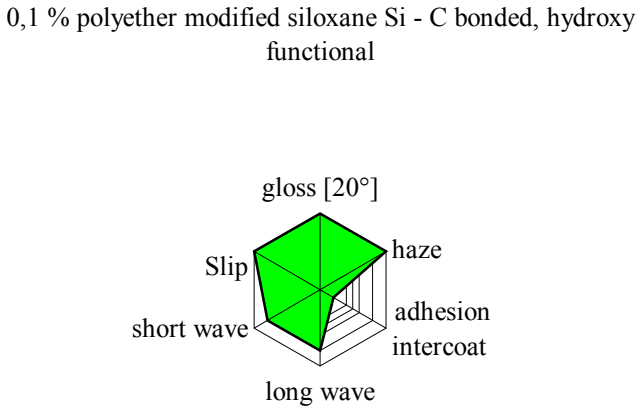

figure 15: results of adding 0,1% polyethermodified siloxane, hydroxy functional to OEM clear coat

The additive used in the next trial is a polyether modified siloxane Si - C bonded, endcapped. In this linear structure is no reactive group.

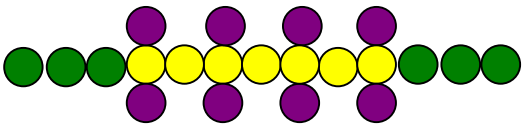

figure 16: structure of polyether modified siloxane Si - C bonded, endcapped

With the endcapped version of the additive the intercoat adhesion is excellent. The additive is not fixed in the surface layer and migrates into the following paint layer. With this example can be demonstrated that the additive must carefully be chosen for a paint system and the special application.

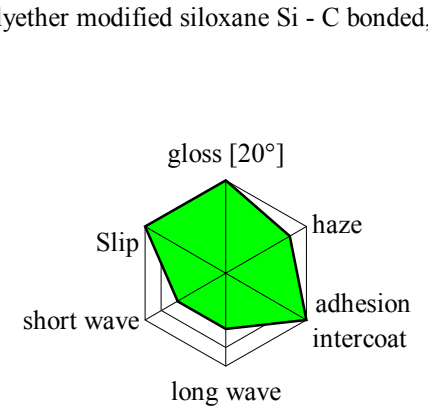

figure 17: results of adding 0,1 % polyether modified siloxane Si - C bonded, endcapped

The result of the trials is a combination of the checked additives. So the greatest fulfillment of the targets is possible. Often not only one additive accomplishes the target. The six properties are clearly improved by adding 0,05 % polyether modified siloxane Si - C bonded, endcapped and 0,1 % acrylic homopolymer to the OEM clear coat as shown in the figure below. The acrylate improves mainly the flow and leveling and the modified siloxane Si - C bonded, endcapped improves gloss and slip.

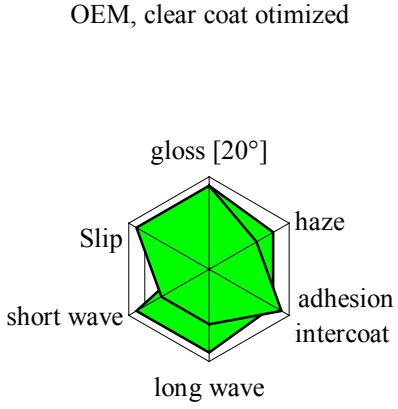

figure 18: optimized OEM clear coat with 0,05 % polyether modified siloxane, Si – C bonded, endcapped and 0,1 % acrylic homopolymer

The same additives are checked in another clear coat system. 2 pack PU clear coats are used for car refinish. The condition of crosslinking are different to the OEM clear coat. Usually it gets no higher temperature than 60°C and the components react after mixing by roomtemperature. First the result of the control is presented.

2 Pack PU clear coat control, without additives

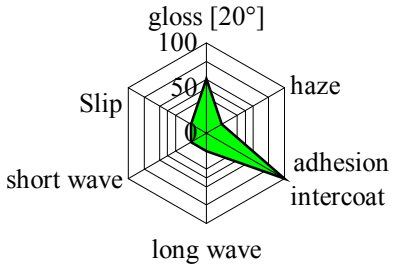

figure 19: control, 2 Pack clear coat without additives

The same additives are checked in these clear coat. The same tendency in testresults was found. The conclusion of these trials is the combination of polyether modified siloxane Si - C bonded, endcapped and an acrylic homopolymer. Adding these combination to 2 pack clear coat the optimum in improvement is reached.

additive combination, o,1 % acrylic homopolymer and 0,05 % polyether modified siloxane Si - C bonde, endcapped

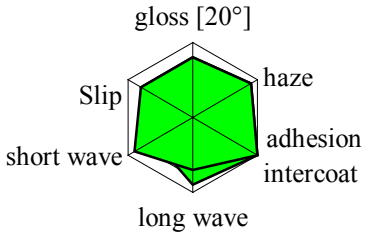

figure 20: results of adding 0,05 % polyether modified siloxane Si - C bonded, endcapped and 0,1 % acrylic homopolymer

SUMMARY AND CONCLUSION

These study demonstrates clearly the importance of polyether modified siloxanes. Because of the increasing demands in optical appearance in the automobile manufacturing flow control agents are necessary. Additional the tendency to thinner applied coating layers call for flow control agents. Without additives the demands of today cannot be satisfied. Today there is a large knowledge developing polyether modified siloxanes for specific tasks. The time of being afraid of siloxanes has come

to an end. Today polyether modified siloxanes are useful helpers to formulate high technical coatings.

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