Macromol. Symp. ***187*****,** *853–860 (2002)*

Evaluation of the Scratch Resistance with Nano- and Multiple Scratching Methods

Rolf Nothhelfer-Richter, Eugen Klinke, Claus D. Eisenbach*

Forschungsinstitut für Pigmente und Lacke e.V., Allmandring 37, 70569 Stuttgart, Germany

Summary: The scratch resistance of automotive clear coats was investigated by a single and multi scratch test procedure. New data characteristic for the reflow capability, the scratch hardness and the lateral scratch resistance were generated and evaluated. A correlation between single and multi scratch data was established.

Keywords: scratch resistance, nano-scratch test, multi-scratch test, polymer coatings, automotive clear coats, AFM

Introduction

Automotive coatings are expected to fulfil high quality and performance requirements in both the protection of the substrate and the optical appearance. The optical quality of the clear coat is impaired by damages extending only a few micrometers below the surface. Therefore single (nano) and multi scratch tests have been developed and employed in order to get a better understanding of the so-called marring process. It has been shown that the data obtained with a nano scratch test instrument, i.e., that the mechanical load at which lateral cracks occur alongside the scratch trace can be taken to rate the mar resistance [1 - 5]. However, as it will be shown in this paper, there are more characteristics to be extracted from the nano scratch test, which allow a better evaluation of the scratch resistance. In this context, the problem of how to correlate the nano scratch test data with multi scratch experiments like the Amtec-Kistler car wash simulation, the Rota-Hub scratch tester or others will be addressed as well.

Experimental

Samples

Five different automotive clear coats have been investigated. All samples were cured at

 CCC 1022-1360/00/$ 17.50+.50/0

designated curing temperature (index b) and also at a lower (index a) and a higher (index c) temperature. Curing temperatures and curing times are given in Table 1.

Table 1. Compositional characteristics and curing conditions of the samples.

Sample No.	Sample	Curing Agent	Curing Time [min]	Curing Temp. [° C]
1a	1 K			120
1b	onepack	melamine	17	140
1c	standard acrylic			160
2a	1 K			115
2b	onepack	melamine/IPDI	30	135
2c	standard acrylic			155
3a	2 K			70
3b	twopack	HDI	30	80
3c	acrylic			100
4a	2 K			115
4b	twopack	HDI	20	135
4c	polyester			155
5a	2 K			110
5b	twopack	HDI / IPDI	30	130
5c	polyester/polyacrylate			150

Scratch test devices

The single scratch test has been carried out with a CSM Nano Scratch Tester (NST); the multiple scratching was generated by using a Bayer Rota-Hub (RH) instrument. For details about methods it is referred to the literature [2, 6].

Results and discussion

The Nano-Scratch Test (NST) provides detailed information about the generation of a single scratch. An indenter of Rockwell geometry (conical, die angle 90°, tip radius 2μm) is pushed with increasing load into the sample, which is moved with a constant velocity. During the scratch process data of the tangential F_t and the normal force F_n as well as the depth are recorded. The penetration depth d_p of the indenter and the remaining depth of the scratch (residual depth d_r) are calculated using the data of a surface scan with minimal load before (prescan) and after (postscan) the scratch (Figure 1). The postscan is performed about one minute after the scratch. From this experimental procedure not only the critical values of the normal force at the first crack and the residual depth at the (arbitrary) value of 5 mN of the normal force can be taken, but additional information can be extracted from the measured curves.

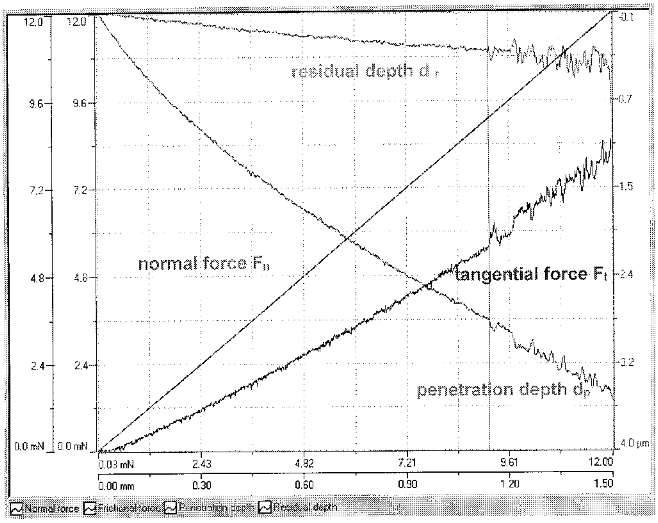

Figure 1. Original data curves as generated in the nano scratch measurement.

The scratch resistance will increase with increasing reflow capability of the sample. Therefore we define a reflow capability value $R = (d_p - d_r)/d_p$. This value will become one if the residual depth becomes zero, i.e. there is no remaining scratch observed. If there is no reflow at all, R will become zero. In Figure 2 the R-curve of sample 3b is shown as a representative example; a smoothed R-curve (named R_m), which is calculated by an error weighted averaging, is depicted besides the experimental curve. The R-curve reaches a plateau above a normal force F_n of only a few millinewtons. This reflow capability remains constant despite the occurrence of lateral cracks after a critical load of about 18 mN has been exceeded; the crack formation is reflected by the rapid fluctuations of the curve.

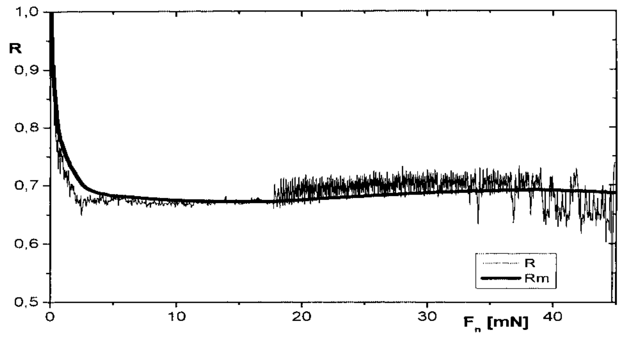

Figure 2. Reflow capability R and averaged R_m of the coating 3b (Table 1) as a function of the applied normal force F_n in the nano scratch test.

From these findings it can be concluded that the occurrence of cracks is not affecting the short time reflow capability of the sample. On the other hand, the long time reflow capability and the annealing of the sample at elevated temperatures will be affected by crack formation.

Some authors state a correlation between scratch resistance and micro hardness [7, 8]. From the nano scratch data a micro hardness $H = F_n / \frac{1}{2} A_c$ can be calculated by dividing the applied normal force F_n by the area of the indenter contacting the coating during the scratch formation (assumed to be half of the total surface area A_c of the conical shaped indenter). In a similar manner the resistance against the lateral translation Z can be defined by $Z = F_t / A_s$, where A_s is the cross-section area of the cone. Both areas can be calculated from the penetration depth using the geometric data of the indenter.

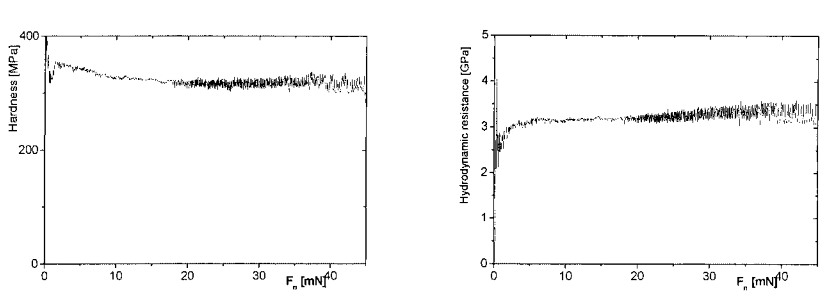

Figure 3. Micro hardness H and hydrodynamic resistance Z as obtained from nano scratch test of coating 3b.

The H and Z values show a plateau as well (Figure 3), which is also very little affected by the occurrence of cracks. Therefore the value taken at the first crack can be taken as characteristic value.

For comparison, the universal hardness was measured with a Fischerscope H 100 micro-indenter fitted with a Vickers indenter at a penetration depth of 3.5 μm (to avoid influence of the substrate). The samples show a good correlation (Figure 4); the offset is presumed to be due to the lateral movement. Further experiments shall clarify this finding. If only a ranking of samples shall be achieved, the nano scratch hardness will be sufficient.

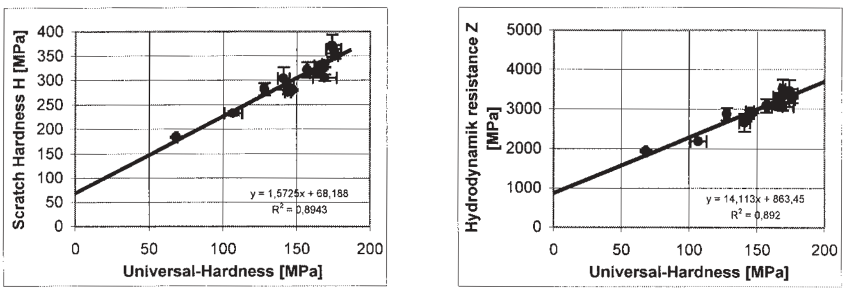

Figure 4. Correlation between scratch hardness and universal hardness for different clear coats.

The data extracted from the NST single scratch experiments are related to the Rota-Hub (RH) multi scratch test data. The scratch resistance of the coating as tested in the RH multi scratch test procedure is evaluated by the gloss loss measured before and after a multi scratch experiment. From the two gloss values the residual gloss is calculated in percent values by dividing the gloss after scratching by the gloss before scratching.

The scratch resistance is expected to increase with increasing hardness and with increasing reflow capability. A plot of R_m versus H is shown in Figure 5, where the residual gloss is indicated by different gray scaling of the points. One expects the points with high residual gloss (high scratch resistance) to lie in the upper right corner and the ones with low residual gloss to lie in the lower left corner. The results of our samples do not meet this expectations, although within the same chemical system a trend can be determined.

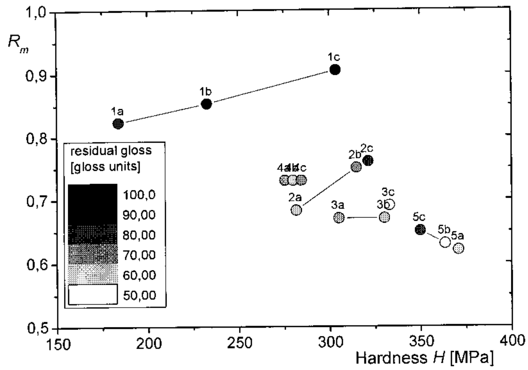

Figure 5. Reflow capability R_m versus scratch hardness H of different coatings (labels s. Table 1); the residual gloss after the multi-scratch experiment is illustrated in the filled data symbols by the gray-scaling.

About ten minutes after the scratch experiment an AFM-image was taken at the 5 mN normal force position. From this imaging the depth and the width of the remaining scratch can be obtained. As schematically illustrated in Figure 6, the scratch widens during the elapsed time (about 10 min. in this experiments) due to reflow processes. The widening can be expressed by the angle α_r of the scratch as compared to the shaft angle α_p of the indenter. During the scratch process the angle is given by the indenter tip, which has a cone angle of 90 degrees.

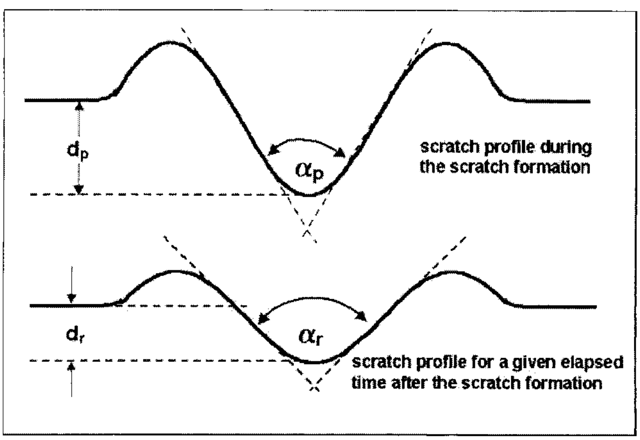

Figure 6. Schematic of the initial scratch profile during the scratch formation with a cone-shaped indentor of the shaft angle α_p and of the residual scratch profile with α_r of the scratch after a given elapsed time.

With increasing angle α_r of the remaining scratch trace, a higher residual gloss was found (Figure 7). This observation is independent from the chemical composition of the coating system. From the optical point of view the reflection of light into other directions than the reflection direction of the unscratched surface will decrease with increasing scratch angle. An angle of $\alpha_r = 180$ degree indicates a totally flat surface, i.e., the scratch has completely disappeared due to the reflow processes. The best samples are only 20 degrees below 180 degree, i.e., $\alpha_r = 160°$.

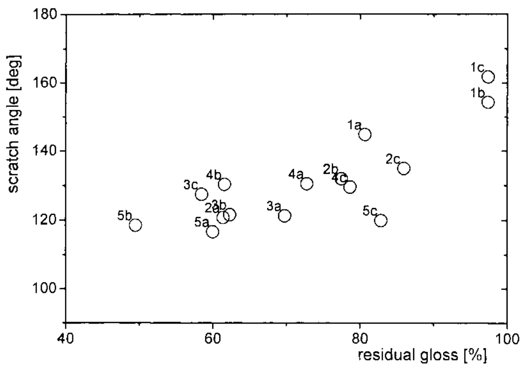

Figure 7. Scratch angle versus residual gloss as obtained for the different coatings (labels s. Table 1).

Conclusions

From the nano scratch experiments new data characteristic for the scratch resistance of the coatings can be extracted. The reflow capability was quantified by introducing a reflow value R which ranges from zero (no reflow) to one (complete reflow (healing)). According to the universal hardness a scratch hardness H and a hydrodynamic resistance Z were introduced. After leveling above a relatively low threshold value of the normal force all three values R, H and Z remain almost constant during the scratch test, even in the presence of cracks. The correlation between the NST data and the gloss measurements of the multi scratched coatings is not yet satisfying and is subject to further investigations. However, a good correlation was found between the scratch angle and the residual gloss.

Acknowledgement

The authors wish to express their thanks to the Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AiF) „Otto von Guericke“ e.V., (AiF). (Grant Nr. 12567) for the financial support.

References

[1] B. V. Gregorovich, K. Adamsons, L. Lin, *XXVIth International Conference in Organic Coatings* **2000**; Vouliagmeni (Athens)/Greece, 81.

[2] E. Klinke, M. Kordisch, G. Kunz, C. D. Eisenbach, *Farbe & Lack* **2002**, *108/4*, 54.

[3] U. Schulz, V. Wachtendorf, T. Klimmasch, *Congress Papers, 6th Nürnberg Congress* **2001**, Vincentz Verlag, 259.

[4] U. Schulz, V. Wachtendorf, T. Klimmasch, P. Alers, *Progress in Organic Coatings* **2001**, *42*, 38.

[5] L. Lin, G. S. Blackman, R. R. Matheson, *Progress in Organic Coatings* **2000,** 40, 85.

[6] E. Klinke, M. Kordisch, G. Kunz, C.D. Eisenbach, Th. Klimmasch, *Farbe & Lack* **2002**, *108*/2, 52.

[7] J. L. Courter, E. A. Kamenetzky, *Congress Papers 5th Nürnberg Congress* **1999**; Vincentz Verlag, 351.

[8] E. Klinke, C. D. Eisenbach, *Congress Papers 6th Nürnberg Congress* **2001**, Vincentz Verlag, 249.