nano resins

TAN US-002: Comparison of various metal oxide nanoparticles grades with Nanocryl products

Account: general study
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All recipe data given in this report is free and may be shared with any customer.

Results Summary

This study compares the scratch and abrasion properties of various metal oxide nanoparticles suspensions with the respective Nanocryl grades in a standard UV curable coatings formulation.
Special attention has been given on the *realistic comparability* between the different metal oxide grades by choosing, adjusting and leveling particles content, photoinitiator and crosslinkable matrix material so that the different S&A behavior can solely be attributed to the different nature and use level of the corresponding metal oxide.
The effect of a special silicone slip additive (BYK 3570) on S&A performance has also been investigated.

The following results have been obtained:

- The competitor Aluminum oxide particles suspensions are in **no way clear**. They are **opaque, milky liquids** that show advanced particulate settling. ***No clear coatings can ever be formulated with these products.***
- The competitor SiO_2 particle suspension does not lead to clear formulations either although this product is somewhat clearer than the Aluminum oxide products. Our corresponding **Nanopol** product does lead to coatings showing absolute **superior clarity**.
- The **abrasion resistance** of the coatings using the aluminum oxide particles suspensions is dramatically **inferior** to our own SiO_2 products.
- The competitor SiO_2 product shows comparable abrasion performance to our Nanocryl/Nanopol materials but **more absolute haze**.
- However, the abrasion resistance of the Nanocryl containing coatings could again be **drastically improved** upon addition of the silicone slip additive BYK 3570. These formulations represent the best coatings in the test and they are by far **superior to all other** formulations with respect to clarity and abrasion resistance.
- The initial steel wool **scratch performance** of the Aluminum oxide particles suspensions seems to be superior to all other formulations in the test field. However, due to the opaqueness of these coatings optical scratch detection might be flawed and results might be compromised.

- The Nanocryl and Nanopol containing coatings show comparable scratch performance, slightly superior to the competitor SiO_2 product. Results regarding different usage levels are not conclusive.
- The silicone slip additive BYK 3570 is expectably not able to further increase scratch performance.

Having said this, it is fair to state that both the competitor Aluminum oxide dispersions as well as their SiO_2 product are no match to our Nanocryl/Nanopol products with regard to coating clarity and abrasion resistance.
The competitor's product performance is clearly inferior. The superiority of our materials can be even further enhanced if the BYK slip additive 3570 is added to the formulation.

Introduction

Raw materials

The competition has repeatedly claimed in the past that their Nanoparticle products have better scratch and abrasion properties than our Nanocryl products due to a special silicone coating that their metal oxide particles apparently have. They also claim that due to this increased S&A performance the use level necessary to improve the finished coating is lower than with other products including ours.
This study investigates the S&A performance of various competitive grades in a true side-by-side comparison with our corresponding grades as well as the effect of a special slip additive.
Special attention has been given on the realistic comparability between the different metal oxide grades by choosing, adjusting and leveling particles content, photoinitiator and crosslinkable matrix material so that the different S&A behavior can solely be attributed to the different nature and use level of the respective metal oxide.

Currently competitor A is marketing the following products:

Table 1: Competitor A metal oxide dispersions: Gradeslate

Competition Grade	Carrier	Viscosity [mPas]	Particle size [nm]	Solids [%]
Grade A – Al_2O_3	Water	25	40	55
Grade B – Al_2O_3	TPGDA	40	40	30
Grade C – Al_2O_3	HDDA	40	40	30
Grade D – Al_2O_3	PM-Acetate	n.n.	20	37
Grade E – SiO_2	PM-Acetate*	10	20	32
Grade F/G/H - ZnO	Water	n.n.	20/40/60	45/45/55

*: Due to compatibility issues the solvent mix also contains Methoxypropanole ratio 6:1

For this study we chose to compare Grade C with Nanocryl C140 and Grade E with Nanopol XP 1184 at two different solids addition levels. Additionally the effect of the silicone slip additive BYK 3570 has been investigated, too. BYK 3570 is an acryl functional polyester-modified polydimethylsiloxane having a iodine number of 26 g/100 g. It is one of four products in a row of BYK silicone based slip additives. The other three are polyether based silicones and are not compatible with our nanosilica materials whereas the compatibility of BYK 3570 with our nanosilica products is very good.

Sample preparation and testing procedures

Testing scratch and abrasion properties of clear coatings is always a difficult task since the methods available are often exposed to subjectivity and the results reproducibility is poor.
Therefore special attention needs to be given on the accuracy of all other factors influencing the scientific reliability of the test results. This includes proper recipe calculation (see below) and proper test procedure handling, e.g. testing all taber panels in one row without any delay. In the literature that is available on the subject of S&A performance testing in combination with particle suspensions two points seem to be repeatedly confused:

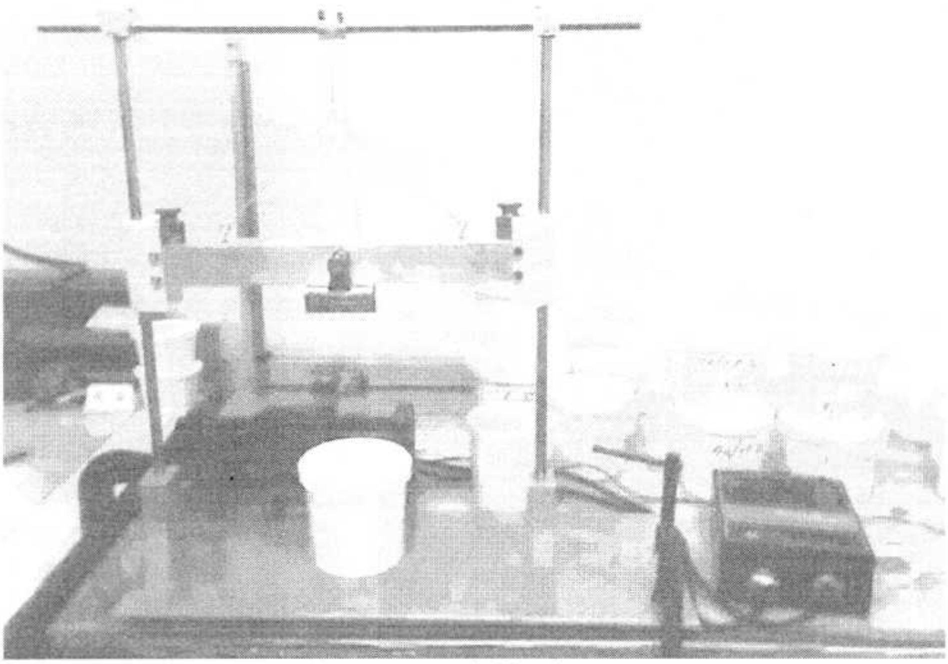
1. Incorrect recipe calculation: When adding carrier-borne particle suspensions to a coating formulation the carrier liquid will be altering the coatings properties, e.g. in the case of HDDA the amount of crosslinkable material is changed upon addition of the particle suspension. This needs to be accounted for when calculating the photoinitiator package as well as the other recipe ingredients.

2. Scratch and Abrasion resistance confusion: Abrasion resistance as measured with a Taber abrader is a wear test and has nothing to do with the initial scratch resistance of a coating. Both properties complement each other. They are not to be confused. Initial scratch resistance is attributed to the surface hardness of the coating and is usually measured with steel wool, Scotch-Brite or pencil hardness testers. It is not a wear test.

All of these methods are more or less subject to the judgment of the individual testing personnel. It is therefore imperative that neither personnel nor equipment is changed during testing. Only by applying these procedures a relatively accurate comparativeness within the test field can be taken as granted.

Since this present study investigates clear coatings the method of choice to determine the amount of abrasion after the Taber procedure is haze loss. The haze of a clear test panel is usually determined using a suitable apparatus (e.g. HunterLab Colorquest II) and is referred to the amount of the percentage of light diffusely scattered compared to the total light transmitted.
The determination of the scratch performance does not allow for the hazemeter to be used since the appearance of first scratches would not alter the overall haze. First scratch appearance can therefore not be picked up by a hazemeter. These scratches need to be detected manually. In this study an automated circular steel wool tester was used to scratch the surface for a defined time with a defined (and increasing) pressure. The amount of pressure that the coating can withstand without showing first scratches is reported.

Another frequent source of inaccuracy in clear coat testing is the different coating thickness. Direct coating thickness determination and control is often difficult to achieve. The sample test panels in this study have been prepared using an automated dipping apparatus (see Picture 1) using controlled dipping speed that allow for a comparable coating thickness of all formulations presuming the formulation's viscosities are the same. This has been accounted for using excess solvent to equalize the viscosities.



Picture 1: Automated test panel dipping apparatus

The following parameters have been applied for preparing the test panels:

Test panel material: PMMA, 4x4 inch, 0.06" thick.
Coating viscosity: 15 cPs @ 25°C. Viscosity has been equalized using excess n-butylacetate.
Dipping speed: 6.5 in/min.
Solvent flash-off: 3 min. @ 120°F.
UV cure: 2 passes @ 300 W/in with 15 ft/min conveyor speed.

Recipes:

It is the scope of this study to directly compare the Grade C (Al_2O_3/HDDA) with Nanocryl C140 (SiO_2/HDDA) and the Grade E (SiO_2/solvent) with Nanopol XP 1184 (SiO_2/solvent) at two different solids addition levels. Additionally the effect of the slip additive BYK 3570 should be investigated.
Table 2 contains the coatings formulations that have been used. The basic control coating consists of a simple mix of Sartomer SR 933 (Dipentaerythrolpentaacrylate) and HDDA initiated by a Ciba Irgacure 500 photoinitiator.

Table 2: Coatings formulation recipes

Ingredient [parts]	02/01 control	02/02	02/03	02/04	02/05	02/06	02/07	02/08	02/09	02/10
SR 933	60	60	60	60	60	60	60	60	60	60
HDDA	67	51	0	60.2	38.3	67	67	67	67	60.2
Grade C -Al2O3/HDDA		23	95.7							
Grade E -SiO2/solvent						21.5	89.5			
Nanocryl C140–HDDA				13.8	57.4					13.8
Nanopol 1184-solvent								13.8	57.3	
BYK 3570										0.4
Photoinitiator I-500	5	5	5	5	5	5	5	5	5	5
Total pts. excl. solvent	132	139	161	139	161	139	161	139	161	139
Total particles parts	0.0	6.9	28.7	6.9	28.7	6.9	28.6	6.9	28.7	6.9
Total particles %	**0.0**	**5.0**	**18.0**	**5.0**	**18.0**	**5.0**	**18.0**	**5.0**	**18.0**	**5**
xlinkable material pts.	127	127	127	127	127	127	127	127	127	127
I-500 per Xlink %	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9

Table 3: Coatings formulation recipes – gross batch amount 600 g

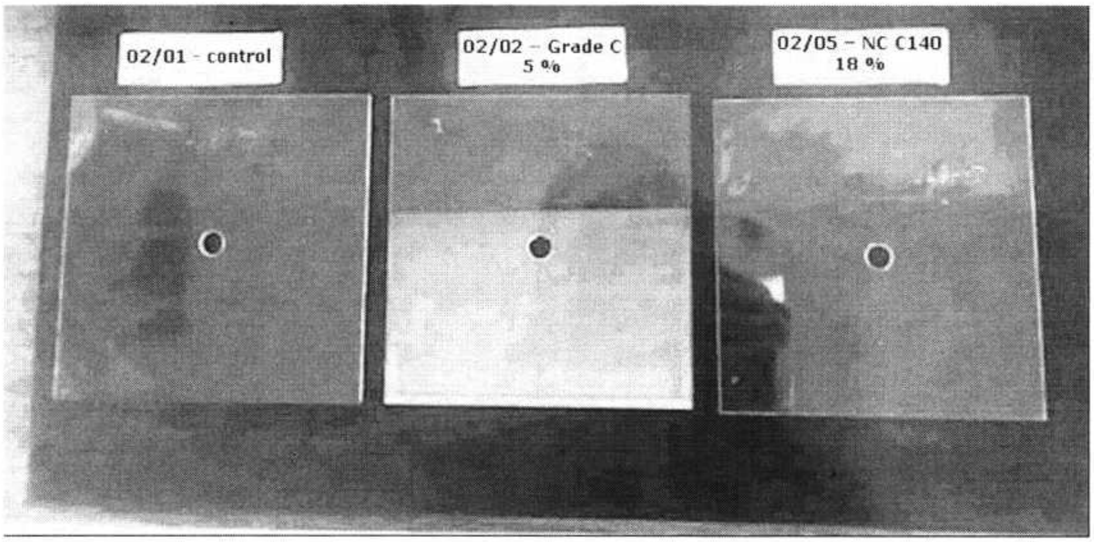
Ingredient [g]	02/01 control	02/02	02/03	02/04	02/05	02/06	02/07	02/08	02/09	02/10
SR 933	272.7	259.0	224.0	259.0	224.0	234.5	162.5	246.9	190.2	258.2
HDDA	304.5	220.1	0.0	259.9	143.0	261.9	181.5	275.7	212.4	259.1
Grade C -Al2O3/HDDA		99.3	357.3							
Grade E -SiO2/solvent						84.0	242.4			
Nanocryl C140–HDDA				59.6	214.3					59.4
Nanopol 1184-solvent								56.8	181.6	
BYK 3570										1.7
Photoinitiator I-500	22.7	21.6	18.7	21.6	18.7	19.5	13.5	20.6	15.8	21.5
Total g excl. solvent	600	600	600	600	600	543	435	572	509	600
Total particles %	**0.0**	**5.0**	**18.0**	**5.0**	**18.0**	**5.0**	**18.0**	**5.0**	**18.0**	**5.0**
xlinkable material g	577.3	548.6	474.1	548.6	474.1	496.4	344.0	522.6	402.5	547.0
I-500 per Xlink %	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9	3.9

Recipe comments:

- The amount of I-500 has been calculated to be 3.9 % on all crosslinkable material in the formulation to account for a comparable state of cure.
- Two solids levels have been realized: 5 % and 18 %. 18 % represents the maximum level that is achievable using the Grade C in this setup due to its low solids contents (30 %).
- The amount of free HDDA in the formulations has been reduced to account for the HDDA added to the formulations by the Grade C and the Nanocryl C140 to ensure proper comparability.
- Formulation 02/10 is identical to formulation 02/04 (5 % SiO_2 via Nanocryl C140) except for the addition of 0.4 pts of the BYK silicone slip additive 3570 to check the effect of this additive.

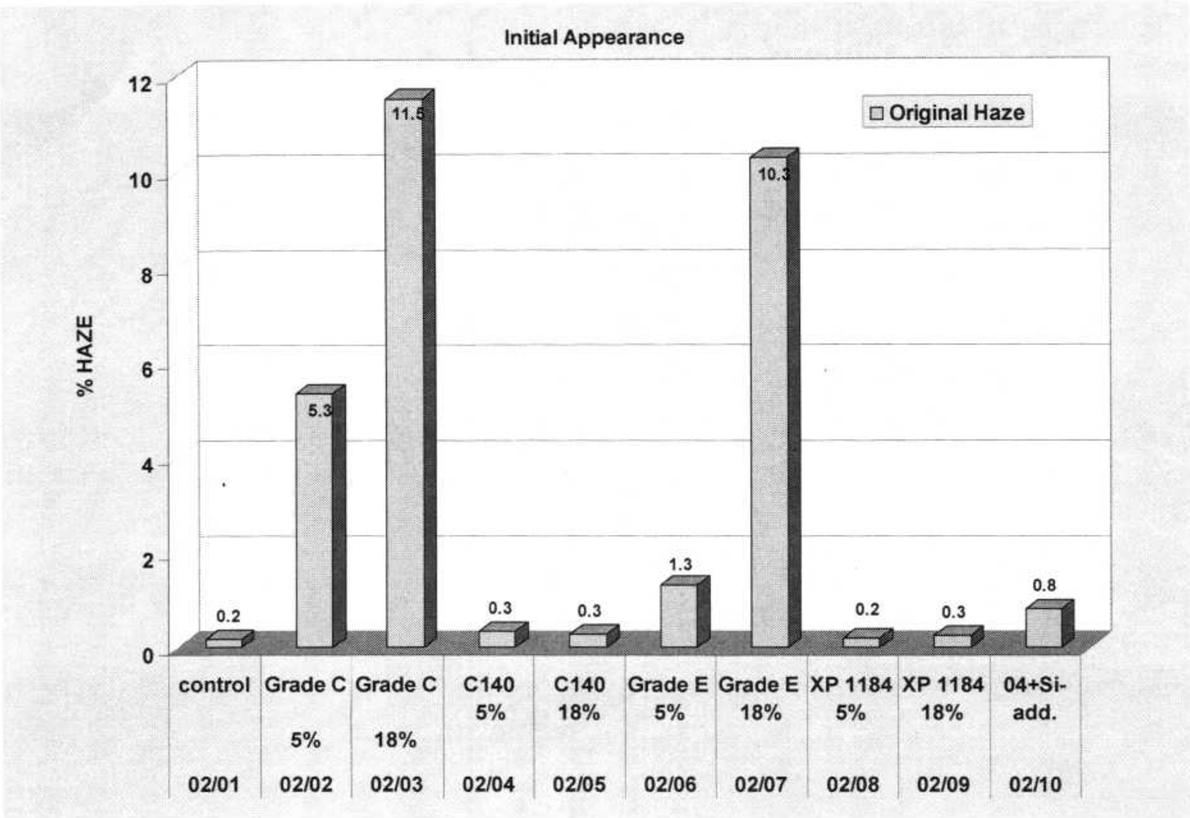
Results:

Initial test panel appearance



Picture 2: Initial appearance of coated test panels

Picture 2 shows how some of the test panels look after they have been coated. It can clearly be seen that the Aluminum oxide product Grade C is not clear at all even at 5 % solids loading compared to the Nanocryl coated panel (02/05) which remains clear even at 18 % solids level.
The optical appearance of the competitor SiO_2 product Grade E is comparably bad which is supported by the initial haze meter readings:

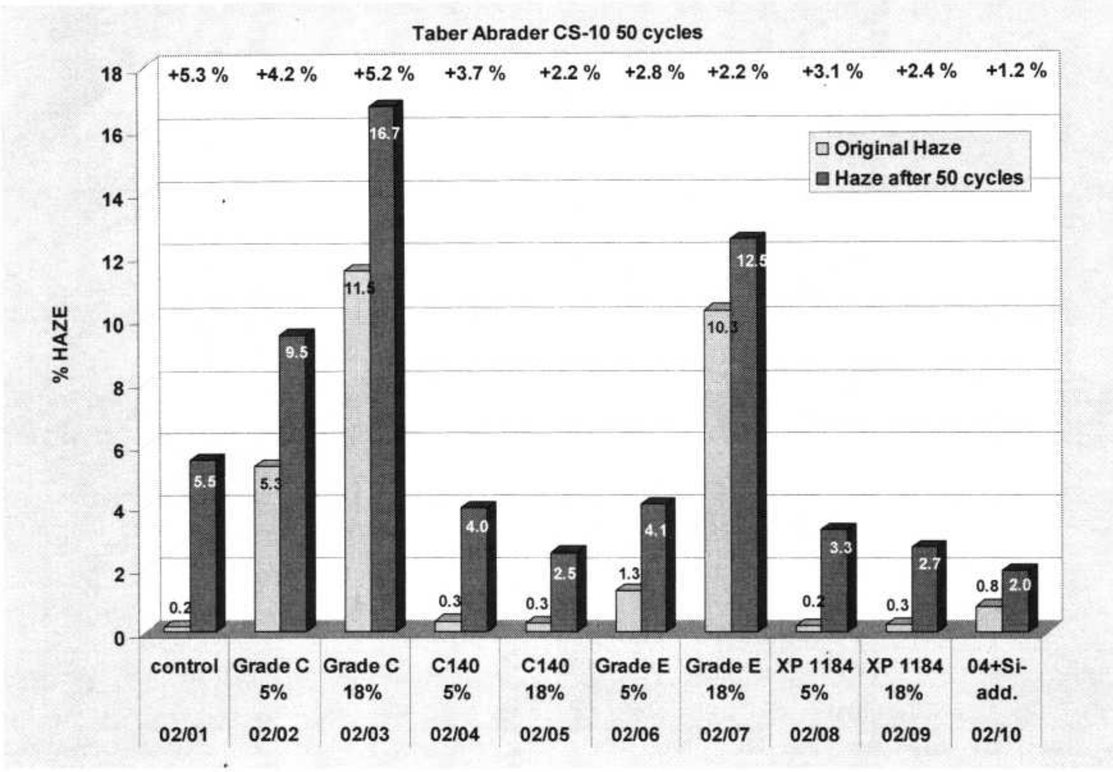


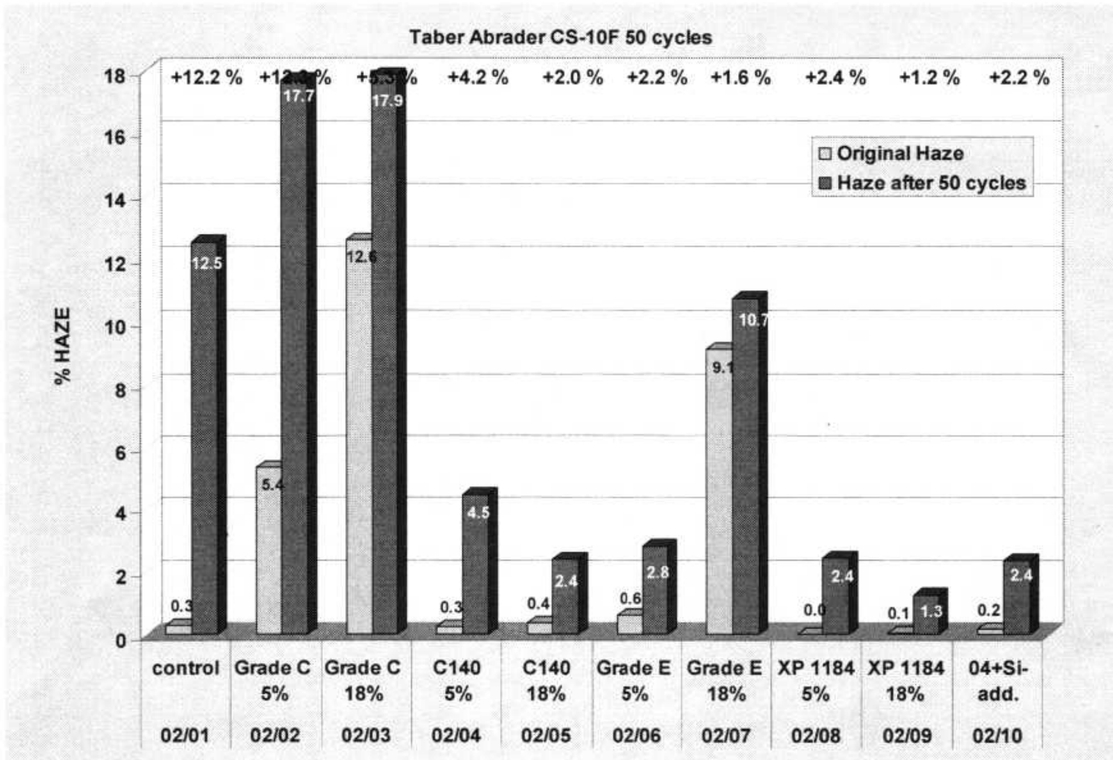
Graph 1: Initial/original haze readings of the coated test panels

The given Hazemeter results are averages of three readings.
The Nanocryl coated panels as well as the ones coated with Nanopol remain remarkably clear and show almost no increase in haze. The competitor SiO_2-product Grade E is inferior which becomes especially visible in higher usage levels. This product as well as the Al_2O_3 product even more so must be considered inapplicable for clear coatings.
It is also noteworthy that the silicone slip additive BYK 3570 does only cause a slight increase in haze when added to the Nanocryl formulation (see 02/10 compared to 02/04).

Taber abrader results

The following graphs illustrate the taber abrasion resistance of the ten coatings. Two sets of experiments were carried out using two different abrading wheel standards: CS-10 and CS-10F. Both standards have been used because some customers prefer the CS-10 over the CS-10F and vice versa. Again, haze has been measured before and after abrading:





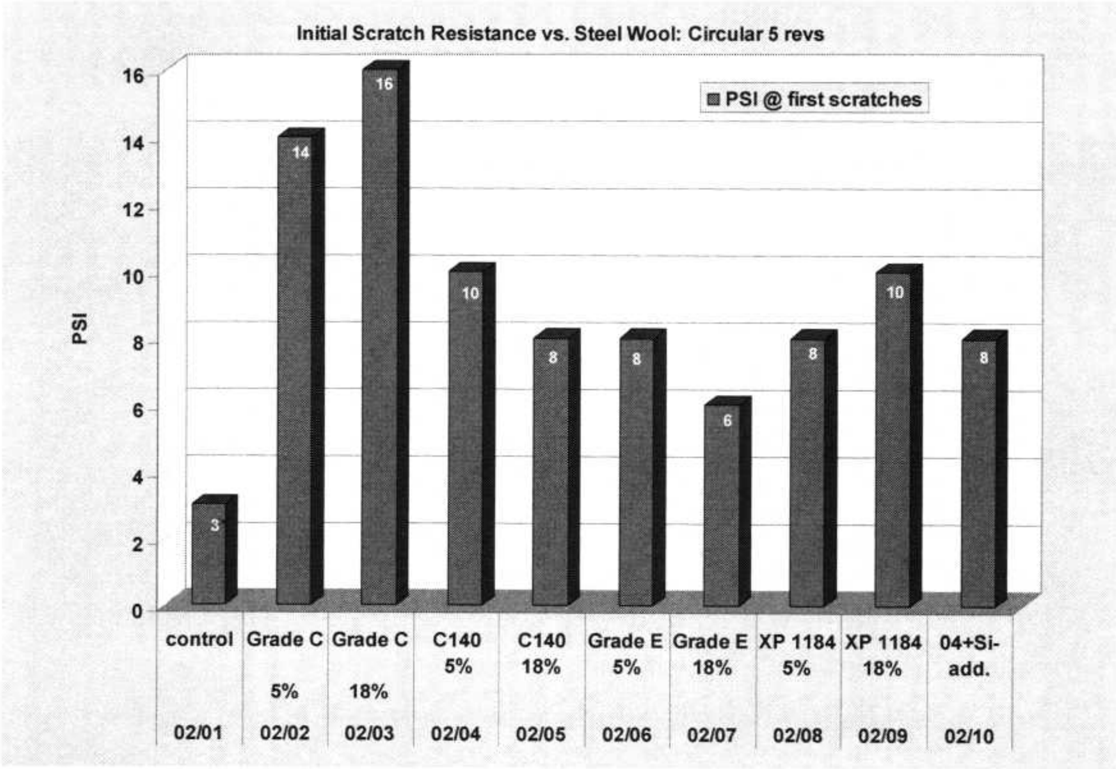
Graph 2+2a: Taber abrasion resistance CS-10 / CS-10F wheels

Several things can be seen:

- In addition to their already very opaque appearance the Aluminum products show very little resistance against abrasion. The coatings become so abraded that almost no change in behavior can be detected between hi and lo particles levels.
- The C140 shows superior performance both in initial haze as well as in haze increase compared to the Grade C.
- The abrasion performance can be further improved by about 50 % by increasing the solids level from 5 % to 18 %. However, the improvement is not linear.
- The competitor SiO_2 product Grade E shows inferior initial clarity. However, the relative increase in haze is about comparable to the corresponding Nanopol 1184 sample.
- The addition of the silicone slip additive BYK 3570 to the 5 % SiO_2 (Nanocryl C140) containing sample leads to yet another 50 % improvement in clarity after abrasion. The performance is comparable to the sample with 18 % particles coming from the NC C140.

Scratch tester results

Graph 3 shows the results of the initial scratch testing shown as maximum pressure that the coating can withstand before first scratches appear.



Graph 3: Initial steel wool scratch resistance

As said before the manual detection of initial scratching can be very difficult. The hazemeter is of no use here since the first tiny scratches would not alter the light scattering enough for the hazemeter to pick up the difference. Nevertheless this is the point where the coating is classified as "scratched".

This is especially true for opaque coatings where the manual detection is even more difficult.

The values reported represent the maximum pressure in psi that can be loaded on the lever carrying the steel wool before the coating becomes scratched. It is determined by increasing the pressure incrementally after each run of 5 circular revolutions with the steel wool sponge. The test panel is inspected visually after each run.

The following things can be deducted from these results:

- The scratch resistance of the coatings loaded with particles is 3-4 times better than of the control coating.
- The Aluminum oxide products seem to have a superior initial scratch resistance. However, as being said earlier, the visual scratch detection of opaque coatings is extremely difficult and might very well lead to false results.
- The initial scratch performance of the Nanocryl and Nanopol coatings is about comparable to the Grade E material with slight advantages for the Nanocryl/Nanopol products.
- It is yet to be understood why the scratch resistance of the NC C140 and the Grade E coatings goes down with increasing particle level. No immediate explanation for this phenomenon can be offered.
- The silicone slip additive BYK 3570 is not able to improve the scratch resistance. This is in good accordance to the different theories and failure modes of scratch resistance and resistance to wear/abrasion on the other hand.

Table 4 summarizes all mechanical test results that have been performed for this study:

Table 4: Test Result Summary

Test results	02/01	02/02	02/03	02/04	02/05	02/06	02/07	02/08	02/09	02/10
	control	Grade C 5 %	Grade C 18 %	C140 5 %	C140 18 %	Grade E 5 %	Grade E 18 %	XP1184 5 %	XP1184 18 %	02/04+ Si-add.
Taber CS-10										
Initial haze	0.2	5.3	11.5	0.3	0.3	1.3	10.3	0.2	0.3	0.8
Haze after 50 cycles	5.5	9.5	16.7	4.0	2.5	4.1	12.5	3.3	2.7	2.0
delta haze	**5.3**	**4.2**	**5.2**	**3.6**	**2.2**	**2.8**	**2.2**	**3.1**	**2.4**	**1.1**
Taber CS-10F										
Initial haze	0.3	5.4	12.6	0.3	0.4	0.6	9.1	0.0	0.1	0.2
Haze after 50 cycles	12.5	17.7	17.9	4.5	2.4	2.8	10.7	2.4	1.3	2.4
delta haze	**12.2**	**12.3**	**5.3**	**4.2**	**2.0**	**2.2**	**1.6**	**2.4**	**1.2**	**2.2**
Initial Scratch psi	**3**	**14**	**16**	**10**	**8**	**8**	**6**	**8**	**10**	**8**