

The Umicore Challenge

Replacing Ca 10 overbased D60 by Ca 5 neutral D60



As you probably remember, a couple of years ago, a problem had risen with the availability of the auxiliary drier Ca 10 overbased in D60. The single manufacturer of the particular acid that was used for the making of this product, decided to shut down production.

At that very moment most of the paint manufacturers didn't have a lot of options. Still alternatives were possible. Chemically the Ca 10 overbased in D60 is a dispersion of colloidal calcium carbonate in a neutral calcium carboxylate at a 50/50 ratio, the carbonate

being formed during the so called carbonatation step.

Tests have shown that the actual auxiliary drier function of calcium comes out of the calcium carboxylate content. On top it's the calcium carboxylate which has the ability to move freely and block active sites on pigments and fillers that are responsible for the absorption of the cobalt drier. In this way the loss of drying action during storage is prevented. Calcium carbonate does not have these features.

Since only 50 % of Ca 10 consists of calcium carboxylate, Ca 5 Neutral must be as active as Ca 10 overbased. Therefore many users preferred the standard neutral calcium drier, Ca 5 N in D60, because of it's superior action as a pigment wetting agent and also as a flow improver for long oil alkyd paint formulations.

The main advantage of the Ca 10 overbased D60 is its price when calculated on the calcium content. Let this be, after reading this brochure, a serious point of discussion.

In fact you could wonder why so many paint manufacturers, after practically being obliged to use Ca 5 N D60, did return to Ca 10 overbased in D60.

In order to convince you of the cost effectiveness of Ca 5 N in D60 in replacement of Ca 10 overbased in D60, we have elaborated several tests on many different paint formulations.

We have siccated 5 different paints once using a mix of cobalt, zirconium and calcium (based on Ca 10 Overbased in D60) and once using a mix of cobalt, zirconium and calcium (based on Ca 5 N in D60).

We have replaced Ca 10 by Ca 5 N weight by weight.

We have applied the paint after 48h storage at room temperature and after 2 weeks storage at

50°C. The drying took place in a conditioned room at 20°C and 50-60% relative air humidity. The needle weight was 10g. The track speed was 3 cm/h. We have applied a wet film of 100µm, two applications per paint. The drying time is given from the start of the measurement.

To test color and gloss, a film of 90µm was applied with a filmograph on a glass plate. The results were measured after 24h and 2 weeks of drying at room temperature. The gloss was measured with a glossmeter at 60°, at 20° for a gloss > 90 at 60° and at 85° for a gloss < 10 at 60°. The value is the average of 4 measurements, 2 in the direction of the applied film and 2 cross-wise. Measurements of L, a*, b* were done with the help of a colorimeter. The value is the average of 3 measurements on different parts of the applied film.

Siccation of the various paint formulations

Product	Ca 10%	Co 10%	Zr 18%	Stabilizer Co 21 %	Co6%Zr9%
Paint A : White floor paint	0.436	0.278	0.691	0.111	
Paint B : White satin egg-shell paint	0.828				0.252
Paint C : Black gloss paint	2.1	1.6	2		
Paint D : White gloss paint	0.595	0.378	0.942		
Paint E : Satin egg-shell varnish	0.772				0.238

Paint A : White floor paint

Drying	Solvent	Dust dry	Tack free	Hard
	USMB Co-Ca-Zr	34'	3h02'	3h35'
	Ca 5 N	42'	3h34'	4h20'
After 2 weeks storage in the oven at 50°C (accelerated aging test)				
	USMB Co-Ca-Zr	25'	1h07'	2h22'
	Ca 5 N	25'	1h13'	2h27'

The drying time is somewhat longer with Ca 5 N at the very beginning but after storage there is no difference at all.

Gloss and color		L	a*	b*	60°
After 24h drying	USMB Co-Ca-Zr	89.3	-3.28	5.95	42
	Ca 5 N	89.03	-3.49	5.47	40
After 2 weeks drying	USMB Co-Ca-Zr	90.4	-1.93	6.05	27
	Ca 5 N	89.86	-2.24	5.25	25
After 9 months drying	USMB Co-Ca-Zr	89.02	0.06	9.22	16
	Ca 5 N	88.15	-0.52	9.16	16
After 2 weeks storage in the oven at 50°C (accelerated aging test)					
After 24h drying	USMB Co-Ca-Zr	89.41	-2.73	4.84	30
	Ca 5 N	89.48	-2.7	4.69	31
After 2 weeks drying	USMB Co-Ca-Zr	90.14	-1.56	4.8	17.5
	Ca 5 N	90.12	-1.67	4.66	17.5

Gloss and color are not affected.

Paint B : White satin egg-shell paint

Drying	Solvent	Dust dry	Tack free	Hard
	USMB Co-Ca-Zr	32'	3h55'	6h57'
	Ca 5 N	29'	2h59'	4h59'
After 2 weeks storage in the oven at 50°C (accelerated aging test)				
Ca 5 N	USMB Co-Ca-Zr	26'	10h59'	14h27'
	Ca 5 N	26'	8h01'	11h13'

Ca 5 N gives even better drying in both cases.

Gloss and color		L	a*	b*	60°
After 24h drying	USMB Co-Ca-Zr	93.92	-1.9	1.73	39
	Ca 5 N	93.26	-2.02	1.14	43.5
After 2 weeks drying	USMB Co-Ca-Zr	94.24	-1.82	1.35	23
	Ca 5 N	93.64	-1.9	0.78	26
After 9 months drying	USMB Co-Ca-Zr	93.93	-2.75	6.85	17.5
	Ca 5 N	93.1	-3.05	6.76	19
After 2 weeks storage in the oven at 50°C (accelerated aging test)					
After 24h drying	USMB Co-Ca-Zr	93.93	-1.62	1.49	63
	Ca 5 N	93.5	-1.75	1	57
After 2 weeks drying	USMB Co-Ca-Zr	93.92	-1.72	1.25	38.5
	Ca 5 N	93.62	-1.81	0.93	31.5

The gloss is not affected by the use of Ca 5 N. Only after the aging test, you can notice a lower gloss when using Ca 5 N.

Paint C : Black gloss paints

Drying	Solvent	Dust dry	Tack free	Hard
USMB Co-Ca-Zr	1h03'	2h08'	4h22'	7h38'
Ca 5 N	1h16'	2h45'	6h33'	10h39'
After 2 weeks storage in the oven at 50°C (accelerated aging test)				
USMB Co-Ca-Zr	57'	1h57'	5h22'	12h59'
Ca 5 N	1h01'	2h30'	8h56'	14h41'

The drying with Ca 5 N is slower.

Gloss and color		L	a*	b*	20°
After 24h drying	USMB Co-Ca-Zr	19.93	0.07	-0.14	88
	Ca 5 N	19.92	0.07	-0.15	87.5
After 2 weeks drying	USMB Co-Ca-Zr	20.08	0.07	-0.19	88
	Ca 5 N	20.09	0.06	-0.12	87.5
After 9 months drying	USMB Co-Ca-Zr	20.33	0.11	-0.17	87
	Ca 5 N	20.32	0.15	-0.19	85.5
After 2 weeks storage in the oven at 50°C (accelerated aging test)					
After 24h drying	USMB Co-Ca-Zr	19.97	0.27	-0.15	88
	Ca 5 N	19.93	0.17	-0.09	87.5
After 2 weeks drying	USMB Co-Ca-Zr	20.19	0.19	-0.15	85.5
	Ca 5 N	20.25	0.11	-0.11	86.5

The gloss remains identical.

Paint D : White gloss paint

Drying	Solvent	Dust dry	Tack free	Hard
USMB Co-Ca-Zr	1h38'	4h39'	7h25'	11h19'
Ca 5 N	1h37'	3h58'	8h07'	12h19'
After 2 weeks storage in the oven at 50°C (accelerated aging test)				
USMB Co-Ca-Zr	1h18'	5h58'	9h	16h14'
Ca 5 N	1h24'	7h07'	10h23'	16h47'

The difference in drying time is negligible.

Gloss and color		L	a*	b*	20°
After 24h drying	USMB Co-Ca-Zr	93.05	-1.41	0.48	83
	Ca 5 N	93.2	-1.33	0.42	83
After 2 weeks drying	USMB Co-Ca-Zr	93.47	-0.88	-0.19	79.5
	Ca 5 N	93.51	-0.84	-0.23	79
After 9 months drying	USMB Co-Ca-Zr	92.4	-3.15	10.65	79
	Ca 5 N	92.41	-3.16	11.56	79.5
After 2 weeks storage in the oven at 50°C (accelerated aging test)					
After 24h drying	USMB Co-Ca-Zr	92.92	-1.05	0.53	87
	Ca 5 N	93.14	-1.03	0.63	89
After 2 weeks drying	USMB Co-Ca-Zr	92.94	-0.98	0.07	84
	Ca 5 N	93.27	-0.99	0.31	86.5

The gloss is identical.

Paint E : Satin egg-shell varnish

Drying	Solvent		Dust dry	Tack free	Hard
	USMB Co-Ca-Zr	30'	2h16'		3h44'
Ca 5 N	31'	1h59'		3h14'	
After 2 weeks storage in the oven at 50°C (accelerated aging test)					
USMB Co-Ca-Zr	23'	3h20'		5h21'	
Ca 5 N	25'	3h15'		5h44'	

Drying time is similar.

Gloss and color			L	a*	b*	85°
	After 24h drying	USMB Co-Ca-Zr	66.18	-2	2.29	59
	Ca 5 N	66.58	-1.98	2.27	58	
After 2 weeks drying	USMB Co-Ca-Zr	66.97	-1.81	2.38	48	
	Ca 5 N	66.15	-1.81	2.34	46	
After 9 months drying	USMB Co-Ca-Zr	68.04	-1.2	5.45	31	
	Ca 5 N	68.25	-1.28	5.93	29	
After 2 weeks storage in the oven at 50°C (accelerated aging test)						
After 24h drying	USMB Co-Ca-Zr	65.3	-1.79	1.88		
	Ca 5 N	66.16	-1.73	2.3		
After 2 weeks drying	USMB Co-Ca-Zr	65.42	-1.72	1.95		
	Ca 5 N	65.31	-1.79	2.08		

The gloss is hardly affected.

Measurement of hardness using Ca 10 overbased D60 and Ca 5 N D60

Hardness is Persoz (s) after 9 months	USMB Co-Ca-Zr	Ca 5 N
	Paint A	182
Paint B	145	152
Paint C	169	172
Paint D	73	69
Paint E	161	163

We notice there is no impact.

A second run on a mix of 85% standard long in oil Alkyd with 15% standard hard gel thixotropic Alkyd gives below mentioned results.

The drying took place in a conditioned room at 20°C and 60-70% relative air humidity. The wet film thickness was 75µm. The needle diameter was 3mm and the needle weight was 10g. The track speed was 3 cm/h.

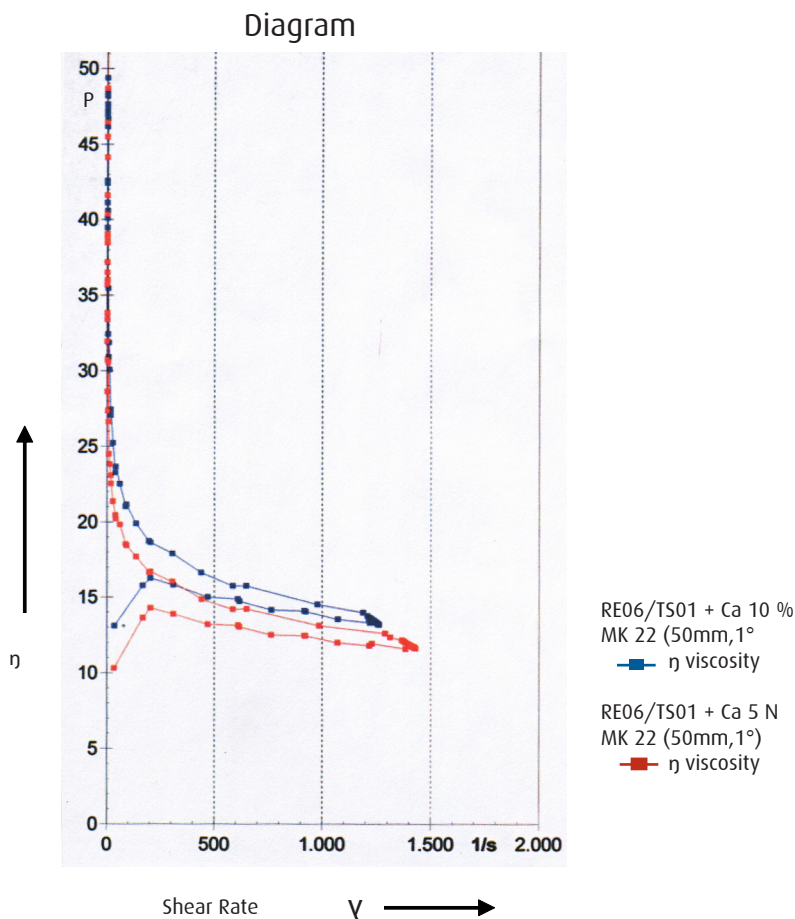
Siccation of standard long in oil alkyd with a standard hard gel thixotropic Alkyd.

Resin sample	Solvent	Touch dry	Hard
85% RE570.06 + 15% TS050.01 + Ca 10	50'	8h55'	11h20'
85% RE570.06 + 15% TS050.01 + Ca 10	45'	9h20'	12h20'
85% RE570.06 + 15% TS050.01 + Ca 5 N	50'	7h40'	10h30'
85% RE570.06 + 15% TS050.01 + Ca 5 N	50'	8h	11h30'

The drying with Ca 5 N is better. Still we observe a higher solvent retention of the thixotropic mix, giving us a softer film.

On these compositions, rheograms were made to assess eventual rheological differences between the two types of siccation.

As can be seen from the graphs, the behavior of both compositions is perfectly similar.



Conclusion

Our intention is to convince you of the price effectiveness of Ca neutral. At the very beginning of this brochure price effectiveness has been described as price per metal content.

In fact we have noticed that price effectiveness needs to be described as price per reactivity or "active" metal content ! Since calcium driers have wetting properties we must admit differences can occur in heavily pigmented paint formulations.

After interpreting the results shown in this leaflet, we can clearly state that a Ca 5 N drier is as effective as a Ca 10 overbased drier. Moreover Ca 5 N brings along a supplementary price benefit.

So please remember

Price \neq Price effectiveness

$$\text{Price effectiveness} = \frac{\text{price}}{\text{"active" metal content.}}$$

We strongly recommend you to test our Ca 5N in your existing paint formulations, in replacement of Ca 10 overbased. You will be amazed by the results !

Should you need more technical information, datasheets or samples, feel free to contact us.



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