

Filler optimization

for road marking paints

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Abstract

The objective of this study was to improve the performance properties of road marking paints by judiciously optimizing the filler system while at the same time remaining in compliance with pertinent legal requirements (version: March 1997).

The study was based on a white and a yellow standard traffic paint. In the relevant formulations, 6 resp. 9 parts of calcite filler were replaced by diatomaceous earth (kieselguhr) or respectively Neuburg Siliceous Earth grade Sillitin Z 89.

For white traffic paints, Silltin V 88 can be recommended as a favorable and less costly alternative to Sillitin Z 89. This new product could not be included in the present study, but it finds already practical use with several manufacturers.

Especially for yellow traffic paints, also Sillitin Z 86 should be considered, a product with a slight yellow tinge and also somewhat cheaper than Sillitin Z 89.

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1 Introduction

A great variety of proven formulations with differing filler combinations is available to the manufacturer of road marking paints. This large choice offers opportunities to develop suitable formulations for specific application requirements.

The objective of the present work was to improve the performance profile of road marking paints by varying the nature of the fillers while maintaining the properties within the limits of legal directives.

2 <u>Experimental</u>

2.1 Raw materials and formulations

Batches of white and yellow traffic paint were prepared based on a standard formulation by varying the filler blend at constant pigment/binder ratio.

	Standard formulation W0 / G0	Batches W1 / G1 and W3 / G3	Batches W2 / G2 and W4 / G4	
	(pbw)	(pbw)	(pbw)	
Cristobalite flour Calcite ¹ Silicate filler	10 34 (33) 	10 28 (27) 6	10 25 (24) 9	

Silicate fillers: Neuburg Siliceous Earth Sillitin Z 89 and Diatomaceous earth (kieselguhr)

 $^{^{1}}$ W = white, G = yellow; the figures in brackets refer to yellow formulations.

White Road Marking Paint						
	Base formulation	6 % Kieselguhr	9 % Kieselguhr	6% SILLITIN Z 89	6 % SILLITIN Z 89	
Batch designation	W0	W1	W2	W3	W4	
Styrene acrylate resin 60 % ATX	24	24	24	24	24	
Texaphor	0,2	0,2	0,2	0,2	0,2	
Soya lecithine	0,9	0,9	0,9	0,9	0,9	
Isobutyl acetate	6,5	6,5	6,5	6,5	6,5	
Aerosil 200	0,2	0,2	0,2	0,2	0,2	
Titanium dioxide	11	11	11	11	11	
Cristobalite flour	10	10	10	10	10	
Calcite	34	28	25	28	25	
Kieselguhr		6	9			
SILLITIN Z 89				6	9	
Toluene	7	7	7	7	7	
Acetone	6,2	6,2	6,2	6,2	6,2	
Styrene acrylate e.g.: Viacryl SC 126/50LG (Cytec Surface Specialties), Arolon SAF 401-BA-60 (DIC Performance Resins) Synthalat A 526 HS (Synthopol).						
Titanium dioxide e.g.:	Kronos 2190 (Kronos)					
Cristobalite flour e.g.:	Farsil 44 (Silmer)					
Calcite e.g.:	Durcal 5 (Omya)					
Kieselguhr e.g.:	Celite 281					

Yellow Road Marking Paint						
	Base formulation	6 % Kieselguhr	9 % Kieselguhr	6 % SILLITIN Z 89	6 % SILLITIN Z 89	
Batch designation	G0	G1	G2	G3	G4	
Styrene acrylate resin 60 % ATX	24	24	24	24	24	
Texaphor	0,2	0,2	0,2	0,2	0,2	
Soya lecithine	0,9	0,9	0,9	0,9	0,9	
Isobutyl acetate	6,5	6,5	6,5	6,5	6,5	
Aerosil 200	0,2	0,2	0,2	0,2	0,2	
Lead chromate	9	9	9	9	9	
Titanium dioxide	3	3	3	3	3	
Cristobalite flour	10	10	10	10	10	
Calcite	33	27	24	27	24	
Kieselguhr		6	9			
SILLITIN Z 89				6	9	
Toluene	7	7	7	7	7	
Acetone	6,1	6,1	6,1	6,1	6,1	
Styrene acrylate resin e.g.: Viacryl SC 126/50LG (Cytec Surface Specialties), Arolon SAF 401-BA-60 (DIC Performance Resins) Synthalat A 526 HS (Synthopol).						
Lead chromate e.g.:	50% HC001 und 50% HC020 (Holland Colours)					
Titanium dioxide e.g.:	Kronos 2190 (Kronos)					
Cristobalite flour e.g.:	Farsil 44 (Silmer)					
Calcite e.g.:	Durcal 5 (Omya)					
Kieselguhr e.g.:	Celite 281					

2.2 Preparation of test batches

Batches of 5 kg each were prepared in a laboratory Dissolver. Final viscosity adjustment was made with acetone, with the silicate fillers requiring 1 to 3 % more solvent than the base formulations.

3 Test methods

3.1 Laboratory tests

The road marking paints were evaluated in the laboratory after application onto glass plates at a wet film thickness of 600 \pm 25 $\mu m.$

3.1.1 Drying characteristics

The influence of the fillers on the drying behavior of the batches represents one of the most important criteria in this study. The drying characteristics, therefore, were determined via two test methods.

Drying according to DIN 53150

In a model test, the time is measured which it takes for the coating to dry to the point that a vehicle rolling over it no longer removes paint from the surface.

Drying behavior of evaporation

This is followed by recording the amount of solvent evaporated from the system with time. The coated glass plates ($30 \times 8 \text{ cm}$) are weighed immediately after the application of the paint, and then the weight loss is recorded until constant conditions are registered.

3.1.2 Skid resistance (grip)

Skid resistance is measured using the pendulum Skid Resistance Tester (SRT) on samples prepared for field trials. The results are given in PTV (equal to SRT) units.

3.1.3 Standard colorimetric values

The standard colorimetric values x and y of samples dried for 72 hours are measured with a spectrophotometer at a light angle of 45° and an observation angle of 0° under normal light type D 65. The samples are tested after a 72-hours drying period.

3.1.4 Abrasion restistance

The coated glass plates are dried for 24 hours at ambient temperature and for further 24 hours at 80 °C, and after cooling tested according to Gardener-Stock.

The samples are mounted in the test instrument at an angle of 45°. Standard sand II is then poured onto them from a glass tube placed at a height of 950 mm. After each 5 kg of sand, a lamp is turned on behind the samples for assessment.

The test is considered complete when the coating has been completely abraded from the surface over an area of 5 mm². The result is expressed in kilograms of sand used.

3.1.5 Day visibility

As an index of day visibility, the standard colorimetric value Y is used.

Determinations were made on laboratory samples (without glass beads) as well as on field trial samples (with beads).

3.1.6 Night visibility

Night visibility was determined on field trial samples with the aid of the Erichsen Reflectometer RM 710.

3.1.7 Viscosity

All batches were adjusted with acetone to a viscosity of 35 to 38 seconds in a 6 mm flow cup (according to DIN 53211, today DIN EN ISO 2431).

3.1.8 Storage stability

Settling tendency

The viscosity-adjusted samples were carried around in a car over a month and over a distance of 1000 km before determining the amount of sedimentation.

High temperature effects

Paint samples were stored in well closed containers over 8 weeks at 80 °C. The amount of sedimentation was then determined, and after homogenization also the viscosity was measured.

3.2 Field trials

In a test area two strips of paint were applied vertically to the direction of travel. The road had an average daily travel volume of 5000 vehicles, and at testing time offered a 3 years old bitumen surface.

The batches were adjusted to a working viscosity of 90 to 95 seconds according to DIN 53211 (\rightarrow DIN EN ISO 2431) and applied using a road marking machine Hofmann H 10 at a wet film thickness of 600 ± 25 µm. Subsequently, the coatings were covered with about 200 g/m² of a mixture of 80 parts glass beads (diameter 100-500 µm) and 20 parts cristobalite sand M72 using a roller spreader.

The coatings were evaluated 3 hours after application (e.g., prior to opening to traffic), after 1 month, 5 months and 10 months (including winter conditions).

3.2.1 Retentivity

The retention of paint is assessed by optical methods and expressed in percentage of remaining marking.

3.2.2 Skid resistance (grip)

Skid resistance was determined as described for the laboratory test, with measurements at the edge and the middle of the lane plus in the driving track.

3.2.3 Day visibility

Day visibility was assessed optically by comparing the sample coatings with two control paints. Control I corresponds to a new coating, Control II represents the legally still acceptable limit.

Rating					
0	excellent, comparable to Control I				
1	slightly poorer than Control I				
2	markedly poorer than Control I, but still good day visibility				
3	satisfactory day visibility, considerably better than Control II				
4	just satisfactory day visibility, comparable to Control II				
5	insufficient day visibility, poorer than Control II				

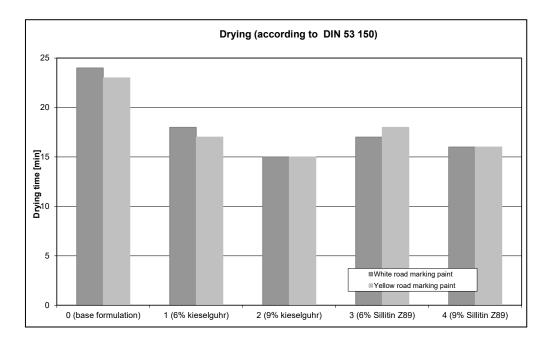
3.2.4 Night visibility

Night visibility was determined the same way as in the laboratory. One measurement each was made at the edge of the lane, in the middle of the lane and in the driving track.

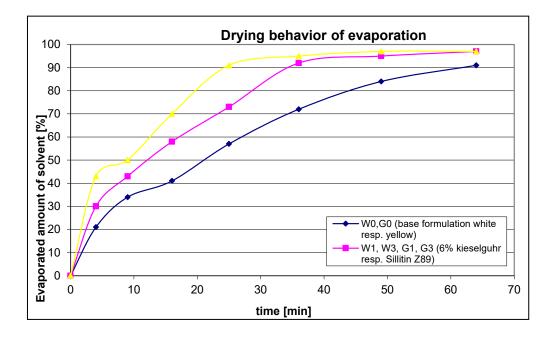
4 <u>Results</u>

4.1 Laboratory tests

4.1.1 Drying characteristics



The silicate fillers markedly accelerate the drying process. The best results were obtained with the higher additions of 9 %.



The benefits of the silicate fillers are particularly evident from the drying profiles: after no more than 25 to 35 minutes, 90 % of the solvent have evaporated. Such a dryness is only reached with the base formulations after about 60 minutes.

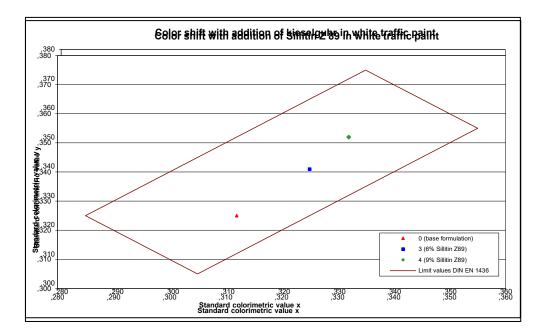
4.1.2 Skid resistance (grip)

All formulations showed a skid resistance between 53 and 56 PTV. This test mainly served to check for uniform application of the markings; it was not expected to find varying results as a function of the filler combination.

4.1.3 Color

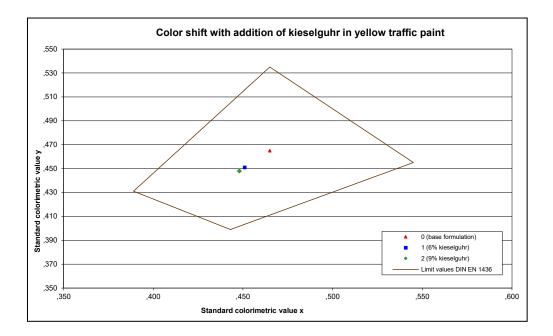
White road marking paint

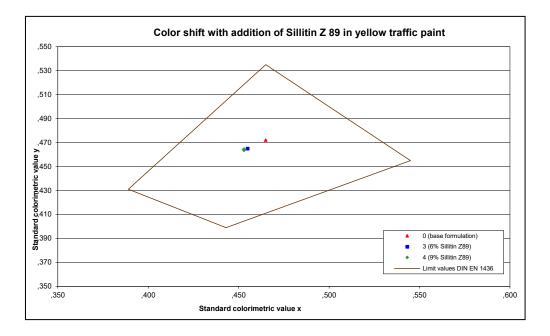
The standard colorimetric values x and y as obtained were compared with regulation limits. All formulations complied with the requirements of DIN EN 1436 (version: 2003).



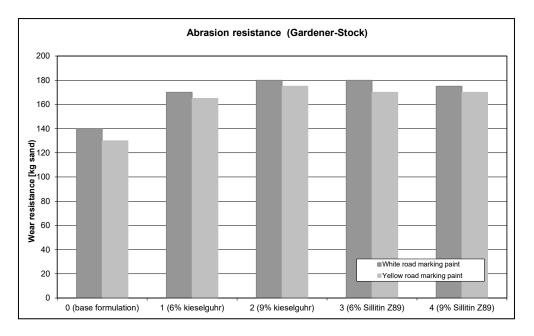
Yellow road marking paint

The standard colorimetric valued as measured were compared with regulation limits. All formulations met the requirements of DIN EN 1436 (version: 2003).





4.1.4 Abrasion resistance



The silicate fillers were able to markedly improve the abrasion resistance. No large differences were detected between low and high doses.

4.1.5 Day visibility

 $\boldsymbol{\beta}$ with beads

White paint	W0	W1	W2	W3	W4
ß without beads ß with beads	88 68	82 62	81 58	83 66	83 65
Yellow paint	G0	G1	G2	G3	G4
ß without beads	63	61	61	62	63

52

53

53

In ZTV-M, the requirement $\beta > 53$ only refers to the white marking with glass beads. ÖNORM B 2440 specifies for white paints $\beta_{without \ beads} > 80$ and $\beta_{with \ beads} > 50$, for yellow paints $\beta_{without \ beads} > 50$ and β_{with} beads > 30. These requirements are met by all formulations tested.

55

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With Sillitin in the white paint a better day visibility with glass beads is obtained compared to kieselguhr. The results of kieselguhr and Sillitin in the yellow paint are on the level of the base formulation.

<u>Note</u> (February 2008): the positive results referring to older standards should no doubt be valid also against the actual standard DIN EN 1436.

4.1.6 Night visibility

The reflection figures measured were between 170 and 230 mcd/m²lx. They largely depend on the application of the glass beads, and were taken mainly to confirm a uniform bead coverage.

4.1.7 Viscosity

The silicate fillers have a higher oil absorption value than calcite. For this reason, the solids content of the batches with silicate fillers was lower by 1 to 2 % as compared with the base formulations at the same flow cup viscosity of 35-38 seconds (solids content around 70 %).

4.1.8 Storage stability

Settling tendency

All batches showed slight binder separation at the surface after the transport test. The samples of the yellow road marking paints with 6 and 9 % kieselguhr exhibited a small amount of easily redispersable sediment, the other batches gave no evidence of sedimentation.

High temperature storage

All batches showed slight binder separation at the surface as well as small amounts of sediment after the high temperature storage test; they all could easily be rehomogenized. The viscosity changes were in the range of \pm 10 %. Only minimal differences could be observed between the individual filler combinations.

4.2 Field tests

4.2.1 Retentivity

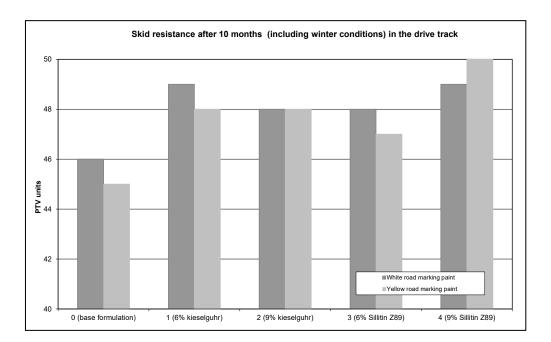
Retentivity is given in % of the total surface area.

White paint	W0	W1	W2	W3	W4
after 10 months	95	90	85	95	90
Yellow paint	G0	G1	G2	G3	G4
after 10 months	90	95	95	85	85

All recipes showed signs of slight deterioration after 10 month (exposed to winter) within the traffic lane, while outside of these hardly any wear could be observed. No significant differences were observed between the individual filler combinations.

4.2.2 Skid resistance (grip)

The PTV figures measured were in compliance with the requirements of DIN EN 1436 (\geq 45 PTV). All trial batches gave better results after 10 months than the base formulation. The best level was obtained with Sillitin at the higher loading.



The findings at the edge and the middle of the lane showed the same trend as the results in the drive track. The lane edge indicated slightly lower grip (skid resistance).

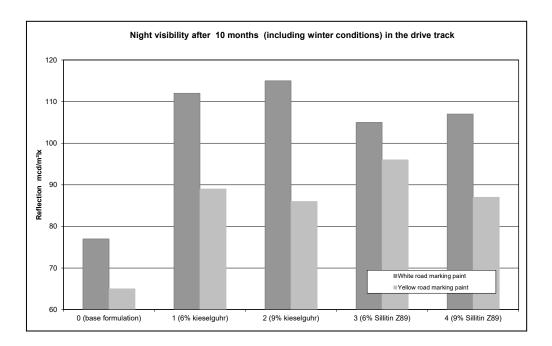
4.2.3 Day visibility

The day visibility was rated between 1 and 3 (cp. 3.2.3), i.e. all batches met the pertinent requirements. No significant differences were found between the individual filler combinations. However, it was interesting to note that, as a result of a self-cleaning effect, the day visibility after 10 months was judged better than after 5 months.

4.2.4 Night visibility

Surprisingly, the batches with silicate fillers after 10 months exposure (including winter conditions) came off superior to the base formulations in the lane areas predominantly exposed to traffic (drive track, but also middle of lane). The formulations containing Sillitin were markedly better than the base control, and similar to kieselguhr.

The results at the edge and in the middle of the lane showed the same trend as in the drive track. At the lane edge, the night visibility was somewhat poorer throughout.



5 <u>Summary</u>

As the study has shown, it is possible to improve the property profile of road marking paints at relatively moderate expenses.

The improved night visibility and skid resistance over the whole period of exposure ensures increased traffic safety. The significant shortening of the drying time allows much faster opening of the marked areas to traffic use.

The partial replacement of calcite by silicate fillers leads to improved traffic paint properties. Already a replacement of 6 % gives rise to noticeable improvements; replacing 9 % imparts further increased benefits. Higher replacement levels of calcite by silicate fillers do not appear practical, as the advantages obtained would not justify the higher raw material costs.

The partial replacement of calcite by Sillitin gave rise to improvements in the following areas:

- Drying
- ► Time to complete dryness (drying profile)
- Night visibility
- Skid resistance (grip)
- Abrasion resistance

Only minor differences were found between Neuburg Siliceous Earth and kieselguhr (see Abstract page 1).

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