The Influence of Selected Synthetic Aluminium Silicates on Physicochemical Properties of Emulsion Paints

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Summary: Synthetic aluminium silicates (AS) consist of amorphous particles with diameters between 5 and 10 µm. They are suited as spacers between the dispersed titanium dioxide pigment particles in emulsion paints, thereby providing an excellent distribution of the pigment. This effect makes a partial replacement up to 50% of titanium dioxide pigments by AS possible. In general the whiteness and the contrast ratio of an AS containing emulsion paints are improved, as well as the scrub resistance in particular cases. The usage of AS also has a favourable influence on the chroma and the brilliance of coloured systems. All these positive effects are primarily controlled by the particle size, porosity, and oil adsorption of the AS. For this reason synthetic aluminium silicates are not just ordinary fillers, but real functional pigment extenders.

Keywords: coatings; silicas; aluminium-silicate; emulsion-paint; whiteness

1. Introduction and History

Precipitated silicas and silicates first entered the coatings and printing inks industries on a sizeable scale around 50 years ago. Synthetic silicas and silicates are now firmly established as matting agents, thickeners, high-grade fillers and pigment extenders. From 1970 to 1999, worldwide production of precipitated silicas and silicates increased from 400,000 tonnes in to 1,100,000 tonnes. In emulsion paints and other decorative coatings, synthetic aluminium silicates are used as a partial replacement for titanium dioxide pigments.

2. Preparation of Synthetic Aluminium Silicates

Starting materials used in the production of precipitated aluminium silicates (AS) are solutions of alkali metal silicates, preferentially sodium silicate, from which amorphous aluminium silicate is precipitated by adding sulphuric acid and aluminium sulphate. Calcium silicate is obtained by using calcium sulphate for the precipitation instead of aluminium sulphate.

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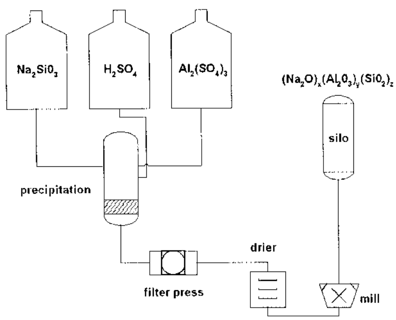


Figure 1. Industrial Production Process of Precipitated Silicas

The following schematic equation (not stoichiometrically balanced) illustrates the precipitation process:

$$\mathbf{Na_2SiO_3 + Al_2(SO_4)_3 + H_2SO_4 \rightarrow (Na_2O)_x\,(Al_2O_3)_y\,(SiO_2)_z + Na_2SO_4 + H_2O}$$

By varying the major precipitation parameters such as temperature, pH, electrolyte concentration and time it is possible to provide AS with different morphology. Through the appropriate selection of precipitation conditions, AS with specific surface areas in the range from 50-200 m^2/g can be produced. The silica suspension obtained in the precipitation process is transferred to the filter press, where the salts formed during precipitation are washed out, and as much of the water as possible is removed. The resulting material is dried and ground in special mills.

3. The Structure of Synthetic Aluminium Silicates

The precipitation process results in the formation of fine, amorphous primary silica particles as determined by x-ray, which associate with other particles to form aggregates and agglomerates. Additional precipitation causes increased agglomerate formation, through the interaction of monomeric or oligomeric silica particles. Within these agglomerates the original primary particles, with an average diameter of about 15-50 nm, remain identifiable.

Figure 2 shows the transmission electron micrographs of four different synthetic aluminium silicates. The aggregates and agglomerates are evident as concretions with an approximate diameter from 0.1 to 1 μm. Synthetic aluminium silicates differ from natural products in several respects:

1. The specific surface area of synthetic products is higher than in natural products.

2. Synthetic products are more uniform.
3. Synthetic products are amorphous whereas natural products containing silica may be crystalline or partly crystalline.
4. Synthetic products possess a greater whiteness than natural products, even when the latter have been cleaned.

Even between the synthesized aluminium silicates, slight coloristic differences are observed. The various products can be distinguished simply by the eye as a result of their different whitenesses. These differences can be attributed to the iron content and the associated yellowing of the material.

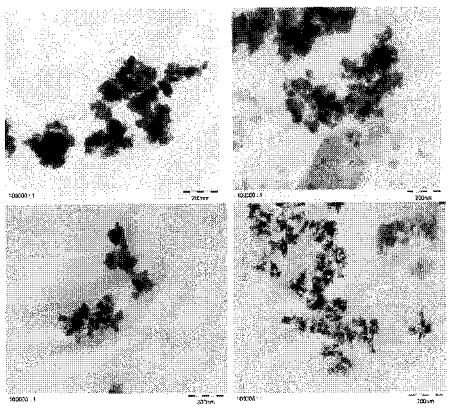


Figure 2. 4 TEM micrographs of different aluminium silicates (on a scale of 100,000:1)

4. Physicochemical Data of Synthetic Aluminium Silicates

Table 1. Physicochemical data

	SAMPLE A	SAMPLE B	SAMPLE C	SAMPLE D	SAMPLE E
Specific surface m^2/g	80	111	51	67	64
Tamped density g/l [1]	288	397	386	228	227
Loss on drying 2 h/105°C % [2]	4.7	8.3	8.0	8.9	7.9
pH, 5% [3]	9.9	7.5	10.4	10.8	10.7
DBP adsorption [4]	160	107	150	160	173
Particle size d50%	7.1	4.7	8.9	5.4	9.1
Particle size d5%	15.2	12.6	20.3	12.2	22.7

	SAMPLE A	SAMPLE B	SAMPLE C	SAMPLE D	SAMPLE E
Standard colour value Y [5]	97.6	98.0	98.2	98.2	97.9
Whiteness (Berger)	96.6	96.7	95.4	95.4	95.4
Fe content	168 ppm	172 ppm	106 ppm	185 ppm	214 ppm

[1] (DIN ISO 787-11), [2] (DIN ISO 787-2), [3] (DIN ISO 787-9), (original material)[4], (DIN 53163)[5]

5. Experimental Section

5.1 Formulas

Table 2. Test formulations for replacement of titanium dioxide pigments by synthetic aluminium silicates

Formulation for an interior emulsion paint	R1 mass %	R2 mass %	R3 mass %	R4 mass %
Water	18.00	18.00	18.00	18.00
Cellulose ether, Tylose MH 6000	0.30	0.30	0.30	0.30
Sodium hydroxide 10%	0.10	0.10	0.10	0.10
Defoamer, Tego 8050	0.20	0.20	0.20	0.20
Dispersant, Dispex N 40	0.20	0.20	0.20	0.20
Dispersant, Calgon N 10%	0.70	0.70	0.70	0.70
Aluminium silicate (samples A to E)		2.5	5.00	7.50
Titanium dioxide (standard, medium and highly treated)	10.00	7.5	5.00	2.50
Talc, Luzenac 00C	7.00	7.00	7.00	7.00
Talc, Naintsch ASE	3.00	3.00	3.00	3.00
Omyacarb 5 GU; $CaCO_3$ d50 = 5 µm	25.00	25.00	25.00	25.00
Omyalite 90; $CaCO_3$ d50= 1 µm	7.00	7.00	7.00	7.00
Sty/Acr or VAc/E binder	16.35	16.90	17.40	17.90
Thickener, Acrysol RM 8	0.10	0.10	0.10	0.10
Defoamer, Tego LA-E511	0.20	0.20	0.20	0.20
Preservative, Actizide AS	0.10	0.10	0.10	0.10
Water	11.85	11.30	10.80	10.30
Total	100.00	100.00	100.00	100.00
PVC	70.0	70.0	70.0	70.0

5.2 Experimental Model

Producers of Emulsion paints want to produce high-quality products as economically as possible. This is one of the reasons why some of the titanium dioxide pigment is replaced by synthetic aluminium silicates. Accordingly, five commercial pigment extenders were compared in two industry standard formulations against three commercial titanium dioxide pigments. These titanium dioxide pigments received different aftertreatments (standard titanium dioxide pigment/low treated, TiO_2 content (ISO 591) ≥ 94%; special emulsion-paint titanium dioxide pigment/medium treated, TiO_2 content (ISO 591) ≥ 88%; special emulsion-paint titanium dioxide pigment/highly treated, TiO_2 content (ISO 591) ≥ 82%). All of the formulations were prepared in three different pigment volume concentrations (PVC = 70%, 75% and 80%) by varying the amount of binder. The experiments were conducted with a styrene-acrylate binder (Sty/Acr) and with a binder based on vinyl acetate-ethylene (VAc/E).

5.3 Experimental Procedure

All of the investigations were conducted in emission free and solvent free interior emulsion paint, whose formulation is given in Table 2. The emulsion paints were manufactured under conventional conditions using a laboratory dissolver whose disc was set at a rotational speed of 7 m/s (2 000 rpm). After the dispersing process, the binder was added with slow stirring. After ageing for one day, the paints were applied using a bar coater (200 and 400 μm slot height) to contrast cards (Byk-Gardner, No. 2801) for optical measurements and to Leneta test panels (P121-10N) to determine the wet abrasion resistance, in accordance with DIN ISO 11998.
The optical properties such as hiding power, whiteness and residual gloss at 85° (sheen) were measured after drying at 23°C and 50% relative humidity (RH) for 24 hours. The various wet abrasion resistance tests were conducted after storage at 23°C and 50% RH for 28 days.

5.4 Results

5.4.1. Hiding Power, Whiteness and Wet-abrasion Resistance

The hiding power is the ability of a dispersion coating to mask large differences in colour and lightness in the substrate. The hiding power should be as high as possible in order to achieve this even at low dry film thickness. The extent of the hiding power can be determined by way of the contrast ratio, comparing the lightness of a white paint on a black substrate with its lightness on a white substrate, according to DIN 53778-3. The hiding power depends on the difference in the refractive indices of the materials used (binder, pigment, filler). The higher this difference, the higher the hiding power. Titanium dioxide pigment provides the largest difference and therefore is the critical factor for the hiding power.

Besides the refractive index, particle size distribution, pigment volume concentration and the degree of dispersion of the pigment, has an effect on hiding power. Effective dispersion of the white pigment and the fillers in the binder is important for its effective deployment. Specifically this effect is achieved by using particularly fine, precipitated synthetic aluminium silicates. These silicates undergo optimum arrangement between the dispersed particles of titanium dioxide and exert, so to say, a spacer effect between the pigment particles. Consequently the precipitated synthetic silicates can optimize the maximum amount of titanium dioxide white pigment in the paint, which is necessary to enhance the hiding power and the whiteness of the formulation.

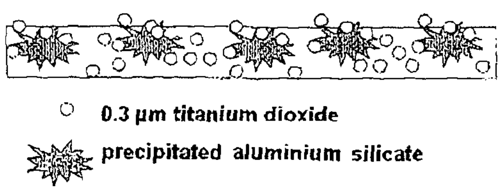
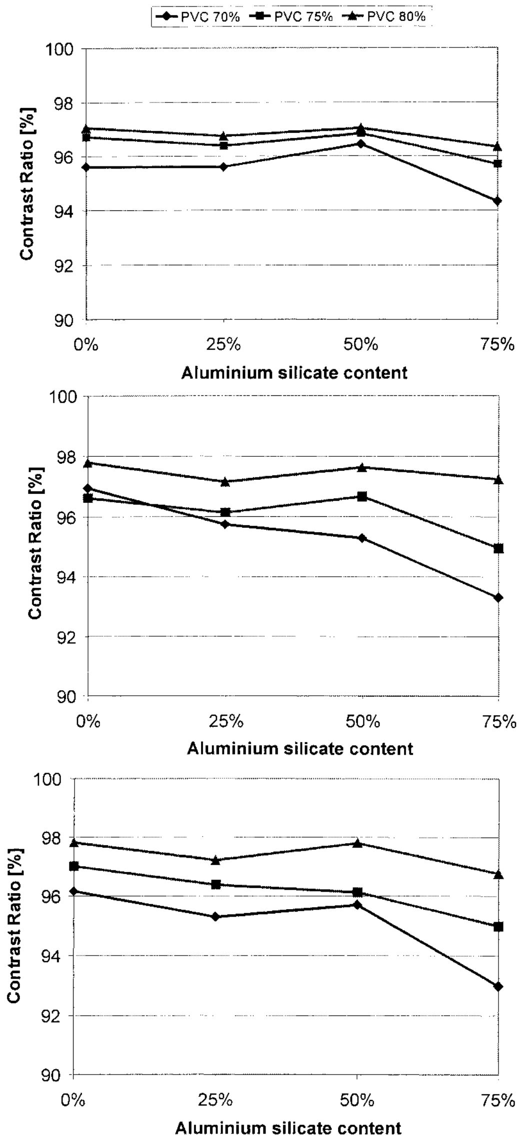


Figure 3. The spacer effect of precipitated synthetic aluminium silicates increases hiding power and whiteness

The fineness of the precipitated aluminium silicate particles gives them a high oil adsorption, thereby lowering the critical pigment volume concentration of the formulation and raising the porosity of the coating system. The refractive indices of calcium carbonate ($n = 1.55$) and aluminium silicate ($n = 1.46$) are quite similar. Both indices lie below the limit that applies to pigments of $n > 1.7$ (DIN 55943 and 55945). Nevertheless, up to 50% of the titanium dioxide pigment present can be replaced by the aluminium silicate without having a negative impact on the contrast ratio (Figures 4a to 4c) or whiteness (Figures 5a to 5b) of the formulation. In fact, in most cases both parameters are improved.

Figures 4a to c. Contrast Ratio (CR) as a function of aluminium silicate content (calculated on TiO_2) and PVC / VAc/E binder



4a) Low treated TiO_2 (high gloss grade)

The formulation based on VAc/E possesses a CR of 95.61% at a PVC of 70%. If 25% of the TiO_2 is replaced by AS (Sample A), the CR remains approximately the same (95.59%). If the AS content is raised to 50%, a maximum of 96.45% is achieved. Only at an AS content of 75% does the CR fall off significantly. The effect on CR is similar at a PVC of 75 or 80%.

4b) Medium treated TiO_2

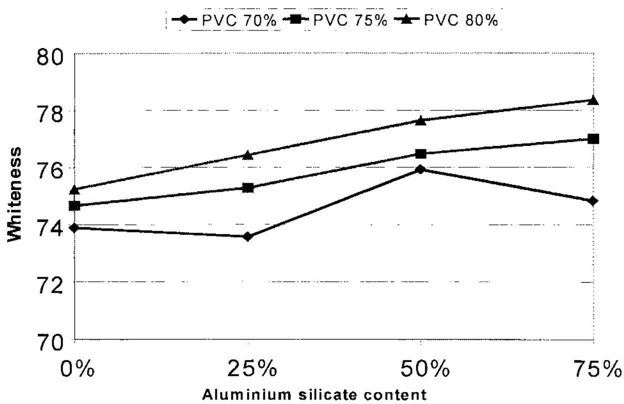
In this case a slight drop in CR from 96.94% to 95.74% or 95.29% (replacement of 25% or 50% of TiO2, respectively) occurs only at a PVC of 70%. At the higher PVCs, the CR remains almost constant at 25% substitution, and reaches a maximum at 50% substitution.

4c) Highly treated TiO_2

Despite high surface treatment of the TiO_2 used, again up to 50% of the pigment can be replaced by AS (maximum again at PVC of 70% and 80%) without a significant reduction in the CR (at 70% PVC from 96.17% via 95.30% to 95.71%).

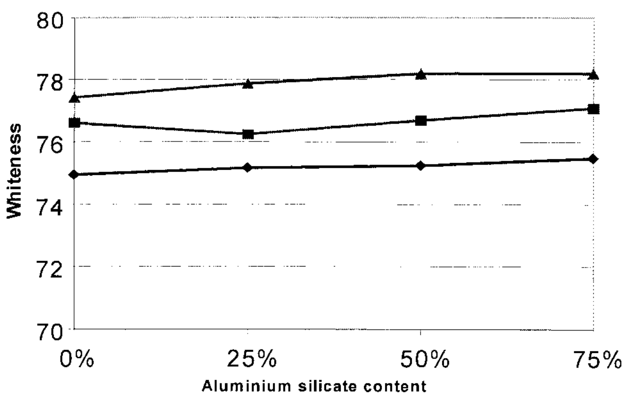
A good filler should be devoid of any substantial inherent coloration, that it, should possess high whiteness, in order not to disrupt the colouring effect of the pigment. Synthetic fillers such as the aluminium silicates perform much more effectively here than natural products. Unlike the latter, they are even capable of raising the whiteness of a formulation, even where there has been a substantial reduction in the level of white pigment, as shown in Figures 5a and b.

Figures 5a and b: Whiteness as a function of aluminium silicate content (calculated on TiO_2) and PVC / VAc/E-binder



5a) Low treated $Ti0_2$ (high gloss grade)

In virtually all cases the whiteness of the formulations is increased.
Here too, our experiments indicate an optimum between the amount of AS and whiteness, which at all PVCs is situated at 50% aluminium silicate content.



5b) Highly treated TiO_2

Contrary to popular belief, an improvement in whiteness can be obtained even in cases of partial substitution of highly treated titanium dioxide pigments. Once again, an optimum is achieved at 50% substitution.

The results of these experiments clearly show that a synthetic aluminium silicate is more than just a common filler, which always of course influences the physical and coloristic properties of a paint, but also serves to increase the volume and hence reduce the costs of a paint formulation.

Aluminium silicates function as an extender, reducing the amount of titanium dioxid pigment, and therefore the cost of the total paint formulation.

In previous experiments (same formulation based on VAc/E, 60% titanium dioxide substitution, PVC = 70%) we compared the AS (Sample A) with two natural calcined aluminium silicates (CC1/CC2) typical for the interior emulsion paint sector. In terms of all their coloristic properties these products were inferior to the synthetic aluminium silicate.

Table 3. Comparison - synthetic AS/natural AS (CC1/CC2)

	STANDARD TiO_2	SAMPLE A	CC1	CC2
Whiteness	74.14	75.8	73.56	74.79
Contrast Ratio	96.93	96.79	95.67	95.65
Particle Size d_{50} [µm]		5	4	3
Sheen (85°)	2.4	2.9	3.1	3.6

It can be seen in Table 3, that the synthetic AS performs better in all coloristic respects than the "natural products". Owing to the somewhat larger particle size of the synthetic AS, the increase in sheen is smaller. However, the sheen can be taken back to the original value with both types of AS. Coarser fillers also bring about a reduction in the binder demand; this should be beneficial to the wet abrasion resistance of the formulation.

The high porosity and oil adsorption of synthetic aluminium silicates reduce the wet abrasion resistance of the formulation. However, the extent of this effect is dependent on a variety of factors such as PVC, titanium dioxide pigment, aluminium silicate content, binder, wetting and dispersing agents. Therefore a standard titanium dioxide pigment or a medium surface-treated one often performs better in terms of wet abrasion resistance than a highly surface-treated titanium dioxide. The investigations also show that the wet abrasion resistance at a PVC of 70% is relatively independent of the aluminium silicate content. However, this does change as the PVC of the formulation goes up. Interestingly, we found that the effect of the binder on wet abrasion resistance can be greater than that of the aluminium silicate content!

Taking into account all of the experimental results and considering the overall properties of the formulation (whiteness, contrast ratio and wet abrasion resistance), additional investigations were conducted using the following combinations: aluminium silicate content = 50%, Sty/Acr binder or VAc/E binder, standard (low treated) or highly treated TiO_2, PVC = 75%

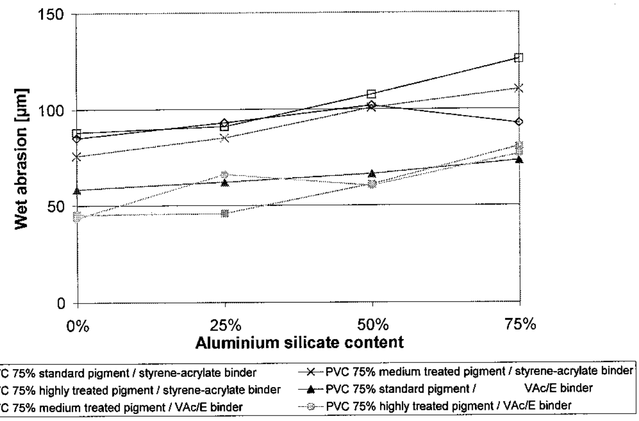


Figure 6. Wet abrasion as a function of aluminium silicate content, titanium dioxide pigment and binder type

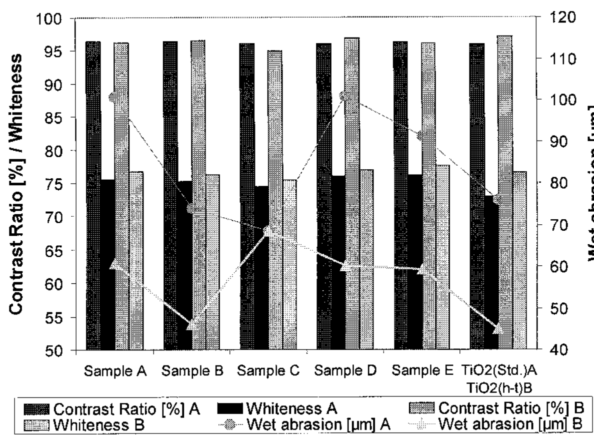


Figure 7. Whiteness, contrast ratio and wet abrasion resistance by ISO 11998 of a formulation based on

A: sty/acr, PVC = 75%, AS content 50%, standard TiO_2 / TiO_2 (Std.) A

B: VAc/E, PVC = 75%, AS content 50%, highly treated TiO_2 / TiO_2 (h-t)

On the basis of these preliminary experiments, the five pigment extenders were tested in the two stated combinations. Essentially, the results from the preceding experiments were confirmed. In formulations based on a standard titanium dioxide pigment, the whiteness was increased in every case and the contrast ratio was almost always improved. In terms of wet abrasion resistance, there are sharp differences depending on the AS used. Particularly, those AS types which do not have the best optical properties still have a favourable effect here and in some cases a very favourable effect, on the wet abrasion resistance which is even improved in comparison with a pure titanium dioxide pigment formulation.

A marked reduction in wet abrasion resistance, on the other hand occurs for the AS which do top the table. This effect is due to the different porosities of the AS types investigated. AS types having a relatively low porosity often equaling the original performance level of the straight titanium dioxide formulation, and in some cases the wet abrasion resistance is even improved by the use of low-porosity AS.

In terms of the partial substitution of highly treated titanium dioxide pigment by the five AS the previous results were confirmed. In the majority of cases the whiteness is increased by using AS. The contrast ratio of the pure titanium dioxide formulation is virtually achieved by all the AS. Again, it should be noted that the effect on the wet abrasion resistance of the titanium dioxide/binder combination used is greater than the effect of the aluminium silicate. Any negative effect of the AS can be more than compensated by choosing a different binder or by using a different type of titanium dioxide pigment.

5.4.2. Colouring Emulsion-Paints containing Aluminium Silicate

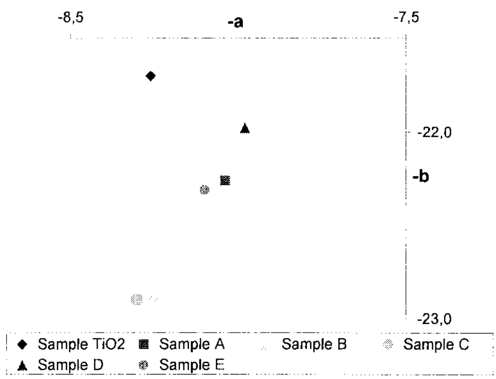
For the colouring tests we used a formulation (see Formulas) with a PVC of 70% based on Sty/Acr. In each case 50% of the standard titanium dioxide pigment was replaced by the tested aluminium silicates. The paint was subsequently coloured with 3% by weight of a cobalt blue pigment paste (Colanyl Oxide Blue Co100, pigment content: 60%). In all of the formulations based on aluminium silicate, the chromaticity of the coloured emulsion paints was raised, so that they appear more blue. Moreover, the AS-based coatings exhibit a higher “cleanness” of shade.

The chromaticity or chroma describes the interaction of the colour values a* and b* and is a measure of the brightness of the coating. A direct relationship exists between the AS pore volume size and the increase in chroma, i.e. a smaller pore volume results in a higher increase in chroma. This phenomenon can be correlated with the spacer effect of the AS. Aluminium silicates with a small pore volume are less efficient in maximizing the titanium dioxide pigment distribution in the paint, since they have far fewer large pores at their surface where the larger titanium dioxide particle could attach. In this case the small cobalt blue pigment particles have a much better chance of finding a site on the AS surface where they can anchor themselves.

Therefore, the number of titanium dioxide particles on the surface is decreased and the blue pigment is maximized, resulting in a coating, that appears bluer and darker → hue. This can be seen in Figure 8 for samples B and C. As seen in Table 1, the tamped densities of samples B and C are higher by about 150 g/l than the tamped densities of the other products A, D and E.

Table 4. Coloristic data for coloured interior wall paints

	L*	Δ L*	a*	Δ a*	b*	Δ b*	Δ E*	C*	h*
Sample TiO_2	77.72		-8.26		-21.70			23.22	249.17
Sample A	77.65	-0.07	-8.04	0.22	-22.26	-0.56	0.61	23.67	250.14
Sample B	76.96	-0.76	-8.25	0.01	-22.88	-1.18	1.40	24.32	250.18
Sample C	76.90	-0.82	-8.30	-0.04	-22.90	-1.20	1.45	24.36	250.08
Sample D	77.96	0.24	-7.98	0.28	-21.98	-0.28	0.46	23.38	250.06
Sample E	77.59	-0.13	-8.10	0.16	-22.31	-0.61	0.64	23.73	250.05



Comparing the Δ a* and Δ b* values for the samples A, D and E, it can be seen that there are no significant differences in relation to the original hue of the pure titanium dioxide formulation (Δ E = 0.46/0.64). Also, small deviations in shade can easily be corrected by minor modifications to the formulation

Figure 8: a*/b* values of the various AS-based formulations in comparison with the pure titanium dioxide formulation / coloured with 3% cobalt blue pigment paste

6. Summary

Synthetic aluminium silicates (AS) undergo optimum arrangement between the dispersed titanium dioxide pigment particles, optimizing their distribution in the paint, which improves the hiding power and the whiteness of the formulation. As a result it is possible to make a considerable reduction of the titanium dioxide pigment in the formulation of an interior or exterior paint. Our experiments showed that a 50% substitution is particularly advantageous in terms of whiteness and hiding power. These advantageous effects of the synthetic aluminium silicate, which lead to cost reductions in the formulation of paints, are also observed when highly treated titanium dioxide pigments are substituted. Synthetic aluminium silicates do not just improve the dispersion of the white titanium dioxide pigment; rather, their use leads to a general improvement in the distribution of inorganic pigments within coloured emulsion paints. It was also found that the chromaticity and colour brilliance of coloured emulsion paints with AS are increased, with both influences being dependent on the porosity of the various AS grades. This also applies to the wet abrasion resistance, which as a result of AS with relatively low porosity in many cases reaches the original level of the pure titanium dioxide pigment formulation, and in some cases is even improved. AS of high porosity have an unfavourable effect on the wet abrasion resistance. The experiments conducted have shown, that this disadvantage can be more than compensated for an appropriate choice of the the titanium dioxide pigment and the binder. Due to the described positive effects, synthetic aluminium silicates are no ordinary fillers, but can be acknowledged as "functional-pigment-extenders".

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