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The effect of the iron oxide in ball clay on the color tone of pigments

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Ball clay is used together with color pigments in order to prepare engobes and manufacture color mixtures, which should shrink between the clay body and the glaze. By a suitable addition of ball clay the pigment is made more plastic and adaptable during the firing process.
The present work investigates how the addition of the color pigment amount together with the iron oxide in clay affects the brightness of the tone changes in the yellow and green pigments. In the experiments the pigments are from the Blythe13 series and the ball clays are chosen among different ECC qualities.
The brightness and the color changes are measured by a Minolta Color Meter. From the measurements it is concluded, that the brightness lowers with a decrease in the kaolinite content. Iron contents below 1.4% do not seem to affect the brightness, but in the case of a high iron content. 2.4 %, a clear decrease is observed. In addition the expected effect of the particle size of the clay on the brightness and color tone changes is investigated.

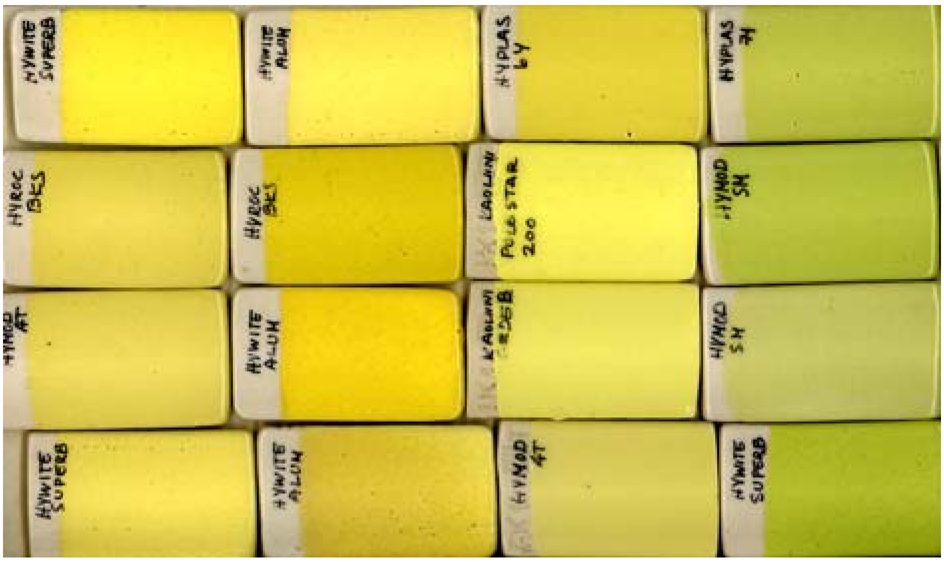

Fig.1: The particle size of the ball clay in test pieces affects the color tone in engobe composition.

1 INTRODUCTION

Clay is used together with pigments when one wants to prepare engobes and use pigments at different temperatures to flexible under glaze color mixtures.
The engobe- and pigment mixture should shrink between the mass and the glaze. By a suitable clay addition the pigment is made more plastic for the workup and in addition more flexible during the burning. The aim of this work is to investigate the suitability of different ECC-clays with pigments. As the main target for the present investigation the color ability of the amount of the iron oxide in the oxide analyses of the ball clays and the particle size distribution have been chosen. In addition to iron oxide also the particle size determines the color quality. The pigments are best seen behind the particles of the masses, if the particles are divided in small and coarse ones.

2 THE SELCTION OF THE CLAYS AND COLORS

The changes in the color qualities of the pigments together with the ball clays have been investigated with light pigments so that the change in color valor should be as clearly as possible observable by eyes.

2.1 Blythe 13-serie under clay colors

Blythe 13-serie colors are used in the test pieces of the slip clays:

Color:	No:	Compound:	Max T:
Citrus	13H5051	PrZrSi	1300 C
Lime Green	13K5056	PrVZrSi	1300 C

2.2 The ECC ball clays chosen for the experiments

Hywite Alum, Hywite Superb, Hyroc BKS, Hyplas 71, Hyplas 64, Hymod PKH, Hymod KC, Hymod SM and Hymod At . In addition the kaolin Standard porcelain has been used as a part of the raw-material. The clays have been chosen among the ECC-clays available at the Department of Ceramics and Glass-art. The aim has been to indicate, by practical experiments, the importance of the percent of iron oxide in the clay analysis compared to the other properties of clay, when you are choosing kaolin and ball clay as plastic materials into engobes and color mixtures.

3 EXPERIMENTAL PARTS

3.1 Amounts of compounds

In the experiments to 5 % and 10 % of the color material has been used. The intension has been to investigate how the addition of color material together with the iron oxide of the clay affect the light yellow and green color changes of the pigments, and to investigate if the right amount is 5 % or 10 %.In the clay mixture 50 % of changing ball clay and 30-35 % have been used while the amount of pigments has varied. To the clay pigment mixtures 10 % of a boron-frit (P2953) has been added, so that the engobe suspension should contain melting a compound and should adhere to the glaze.

Glaze KV1, which is a transparent glaze, the firing temperature 1220^{o}C, has been used. The raw materials for the glazes have been chosen so that they should have a very neutral effect on the colors of the pigments. The frits of the RO-groups of the glaze do not influence on the color of the pigment. The glaze has a viscose melting property and should rather be burned above than below 1200^{o}C.

Empirical formula of the glaze KV1

K_2O	0.216			
Na_2O	0.056	Al_2O_3	0.376	SiO_2 3.445
CaO	0.612			B_2O_3 0.106
MgO	0.115			

The glaze has been sprayed simultaneously on several pieces, so that the thickness of the glaze layer should be the same in as many experiments as possible. The results are the possible to compare to each other.

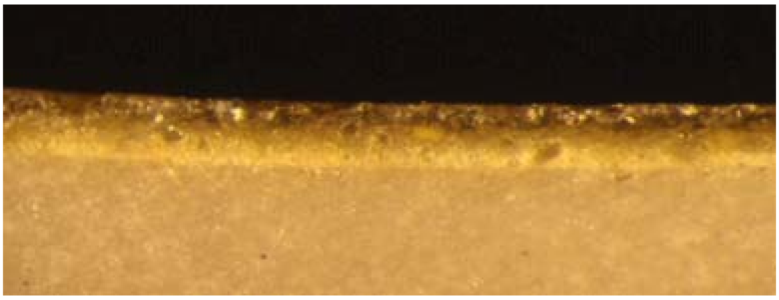

Fig.2: The cross section. In the test piece there is the thickness of the glaze layer on the yellow pigment colored engobe fired 1200^{o}C.

3.2 Colorized clay (engobe) formulations

For each experiment has been made two identical test pieces. They have been prepared in order to control the validity of the firing results. An amount of pigment 5 and10%weight tested with white engobe, different ball clay composition, C-series (Citrus color pigment), and L-series (Lime color pigment) is shown in table 1.

Table 1: An amount of pigment 5 and10%weight tested with white engobe, clay composition, C-series (Citrus color pigment), and L-series (Lime color pigment)

Material[1)]	**C1**	**C2**	**L1**	**L2**
Kaolin,standard p.	35	30	35	30
A/Hywite Superb	50	50	50	50
B/Hymod At				
C/Hyroc BKS				
D/Hywite Alum				
E/Hyplas 64				
F/Hyplas 71				
G/Hymod PKH				
H/Hymod KC				
I/Hymod SM				
Boraxfrit.P2953	10	10	10	10
Citrus/Blyth.13serie	5	10	--	--
Lime /Blyth.13serie	--	--	5	10

1)
AL1 = Hywite Superb Ballclay (=A), Lime green, 5% weight (=1)
BL1 = Hymod AT and Lime green, 5%weight
BC2 = Hymod At and Citrus 10% weight
etc.

3.3 The inspection of the differences of the clays.
The clays which are used in the experiments have been grouped according to their brightness values, because the brightness is directly proportional to the amounts of kaolinite (clay mineral) and mica materials. A special exception is the Hymod SM-clay, which contains a low amount of mica material but contains a high amount of quartz.

Table 2: Kaolinite (clay mineral), mica and iron oxide weight% in mineralogical composition and brightness/whiteness (fired property)

Clay:	Kaolinite%	Mica material%	Brigthtness1240^{o}C	Fe_2O_3
Kaolin*.	84	13	91	0,68
Hywite Alum	77	8	83	1,4
Hywite Superb	70	19	68	1,1
Hymod PKH	71	22	59	1,6
Hyroc BKS	46,3	26,5	52	1,2
Hymod SM*	37**	17*	51	1,4
Hymod KC	56	34	48	1,4
Hyplas 64	45	28	48	0,9
Hyplas 71	40	22	48	0,8
Hymod At	52	31	30	2,4

* China clay Standard porcelain. **The amount of quarts 45 %weight

When you are inspecting the color caused by the pigments it is observed that the amount of iron oxide do not have such a big influence as the amount of mica and quartz relative to kaolinite. The brightness of the ball clay itself, when it is mixed with pigments, tells about the burning color of the clay body and at the same time it is directly proportional to the amount of kaolinite and the efficiency of the color.

4 THE RESULTS

4.1 The amount of color pigments in the clay mixture

In every clay quality one can see the difference between the amount of 5 % and 10 % color. Any clay with 5 % color do not have a better brilliancy that a clay containing 10 % color. A 5 % amount of color gives a pastel touch while 10 % gives a very strong color. It is not favorable to use more than 10 % of pigment, if you no get enough color one should change the clay quality or the amount of clay and add quartz or feldspar instead of clay. The color saturation and brilliancy of color depends on the roughness of the particle distribution that the glaze can wet surface of the clay layer through the particles. The glaze will be a loose layer and the glaze will not reflect the of the pigment particle if the surface layer is tight because of very fine particles.

4.2 Reactions of Citrus and Lime Green color pigments in test pieces

The experiments show that light colors do not interact together. If the mixture has favorable color ability then both pigments are working at the same time. Similarly if the clay mixture is good or bad the results obtained for both when treated with pigments are identical. If a clay formulation gives cold light yellow result it also gives a cold and light green touch. If the clay formulation is difficult and emphasizes the yellow tone it also gives a more yellow and warm color tone of the green color. The experimental results show that both color pigments react in different layers when stacked in oven with Hywite Alum clay. Because of that we have decided to use the clay mixture as a variable and concentrated on the inspection of the experimental results of the yellow color after the testing of the comparable green pigments.

4.3 The effect of pigments in engobe formulations

The brightest yellow color was obtained by the clay Hywite Alum. The next best were the clays Hywite superb and Hyroc BKS. After them come Hyplas 64 and 71. The Hymod PKH acts differently from the Hymod clays and gives a warm sunny yellow touch while the other Hymod clays are pale yellow like the lemon.

4.4 Amount of the iron oxide in the clay analyses

The clay mixtures have been written in superiority in Figure 1 according to their degree of yellow color and color repletion value. The percentage of iron oxide is not directly proportional to the color repletion and coloring, so that a large percentage should rise the degree of yellow color. If this is true the best experimental result is obtained by Hymod At formulation containing 2.4 % iron oxide. On the contrary Hymod PKH containing 1.6 % iron oxide gives a warm yellow color. When the glaze is wetting the color pigments and the surface particles of the mass the amount of iron oxide has only a small effect as a flux (frit) and in increasing the color.

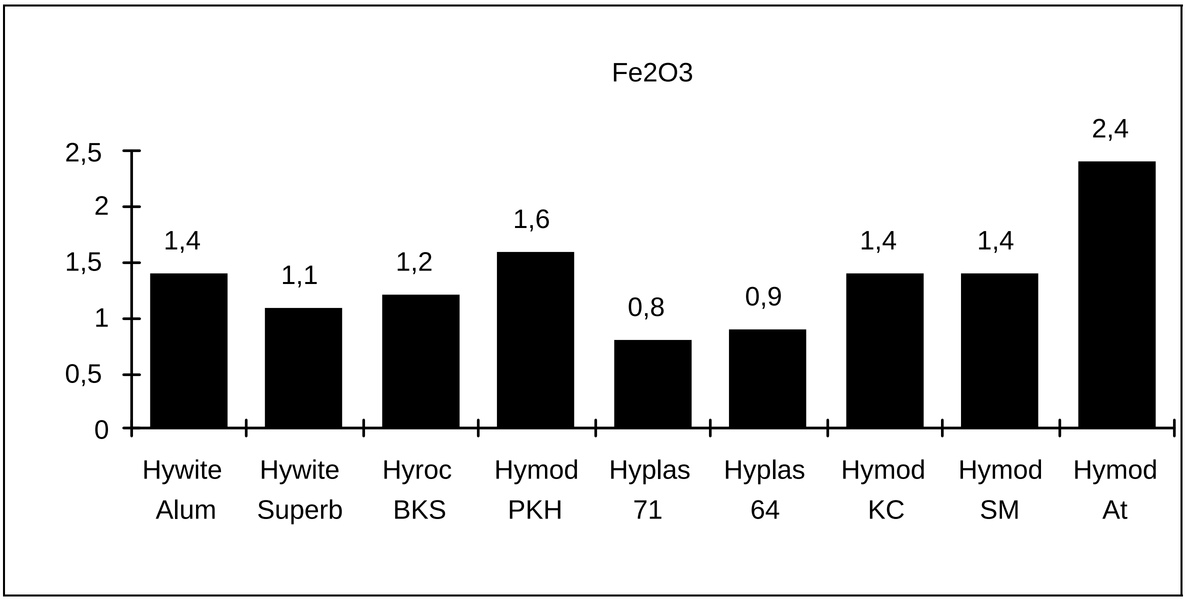

Fig.3: The percentages of iron oxide included in the different clay analyses.

4.5 Particle size distribution of the kaolin (Standard Porcelain), Hywite Superb and Hywite Alum

Because these clay qualities (formulations) contain 30 - 35 % kaolinite its particle size is of importance in cases when the amount of middle size particles (<2ym) is small or large. The particle distributions between two clay mixtures are thus made even. Hywite Alum gives the color glamour of the pigments. In addition to its brightness values it has the most suitable particle size distribution and the sizes <2ym, <1ym and <0.5ym are stressed in the particle distribution.

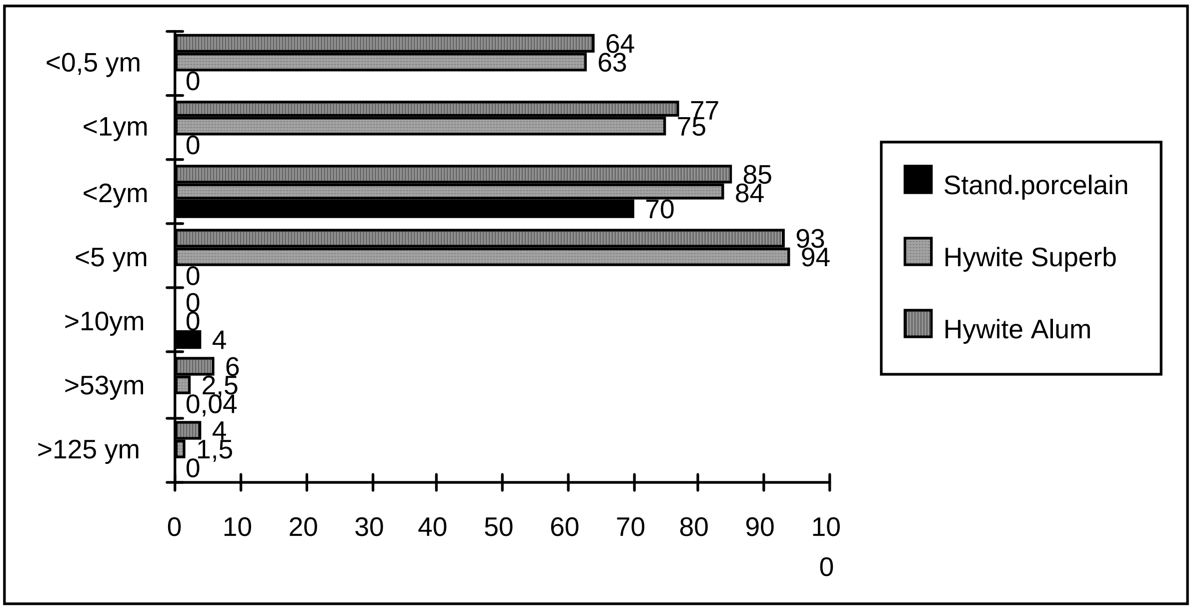

Fig.4: The distribution of the particle sizes of the clays kaolin, Hywite Superb and Hywite Alum.

4.6 The investigation of the Hymod- ball clays
ECC has meant the Hymod- ball clays in the manufacturing tiles and bricks and thus they are together with each other a bit different. For example Hymod At and Hymod KC contain more alkali and are thus adaptable. The shrinkage of the mass between the glaze and the mass is even because of the amount of the fine particles. The glaze does not crack on Hymod At. In addition Hymod At contains more iron oxide, which should be seen as a warm color tone in the yellow pigment mixture. Hymod SM contains an exceptional amount of quartz and least alumina. The glaze is cracking forming a large crackle-image.

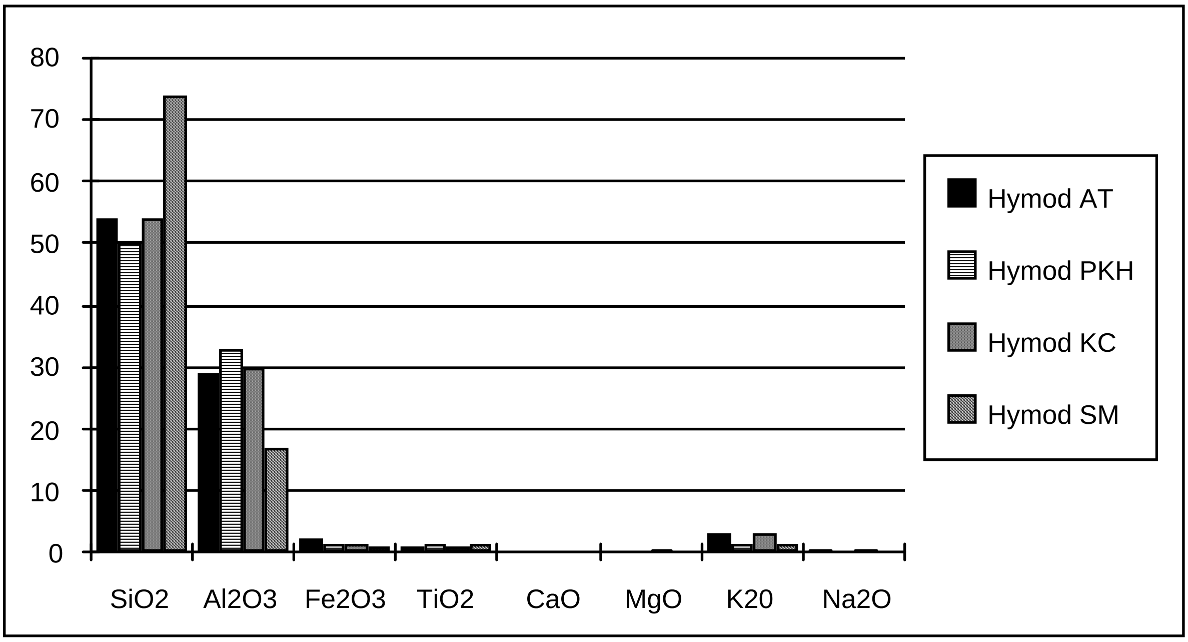

Fig.5: The comparison of the oxide analysis of the Hymod clays used in the experiments. In Hymod SM clay the amount of quartz is exceptional high.. Hymod At and KC contain more alkalis than the other. In Hymod PKH that share of alumina is high.

4.7 Particle size distribution in the Hymod ball clays
Hymod PKH is the most favorable of the Hymod clays to be used with pigments. It emphasizes the glamour of the color, which depends on the high amount of quartz and thus on the high amount of middle size and small particles forming a favorable joint for mass and the glaze. The glaze is able to wet the surface of the colored clay formulation. The coloring is emphasized and the color of iron is seen in the mass.

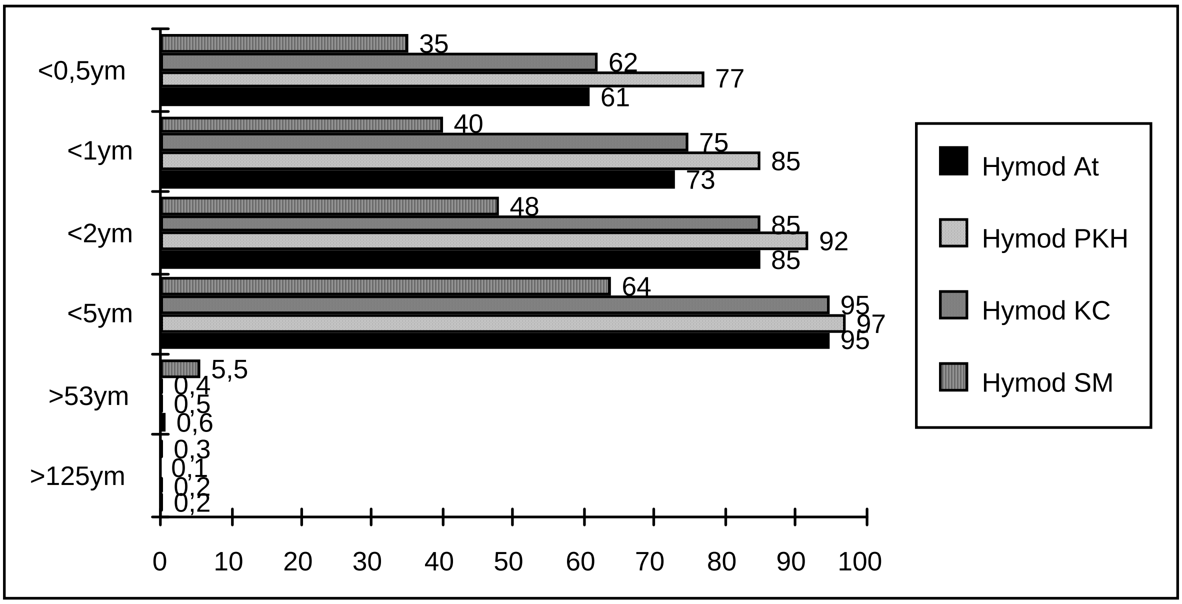

Fig.6: The particle sizes of the Hymod clays. Hymod PKH is finer than the other Hymod clays.

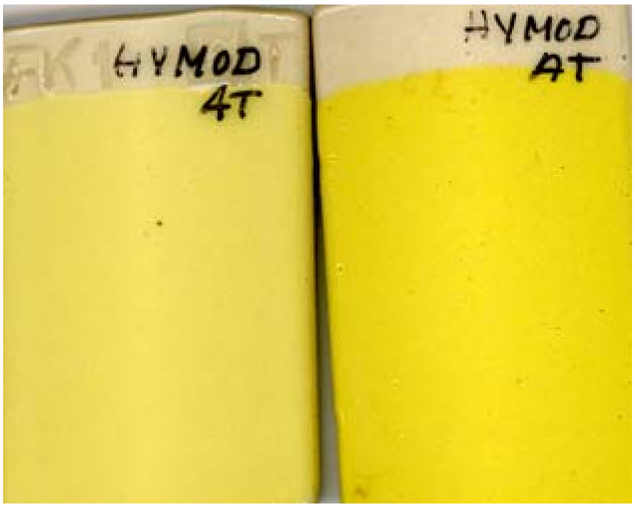

Fig.7: Hymod AT ball clay used with Citrus under clay color 5%weight and 10 %weight.

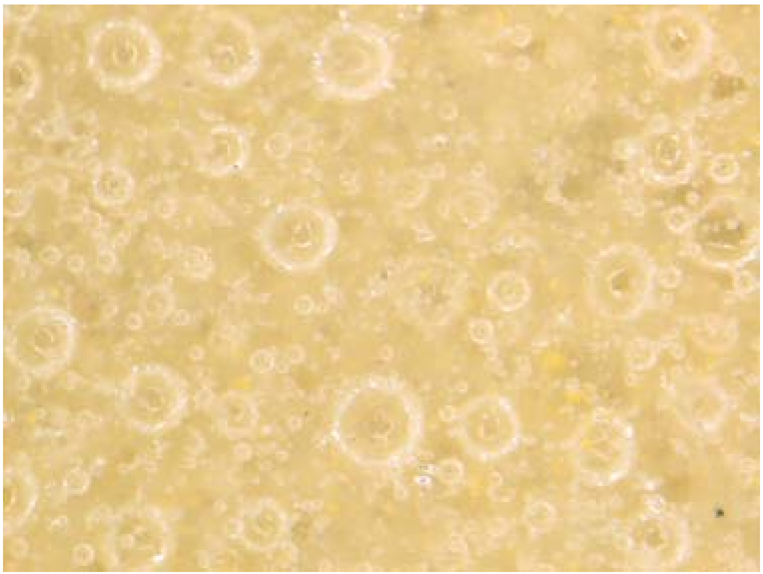

Fig.7a: Microscope enlargement 40. Hymod AT in engobe with Citrus under clay color 5%wight. Test piece fired 1n the electric kiln 1200^{o}C.

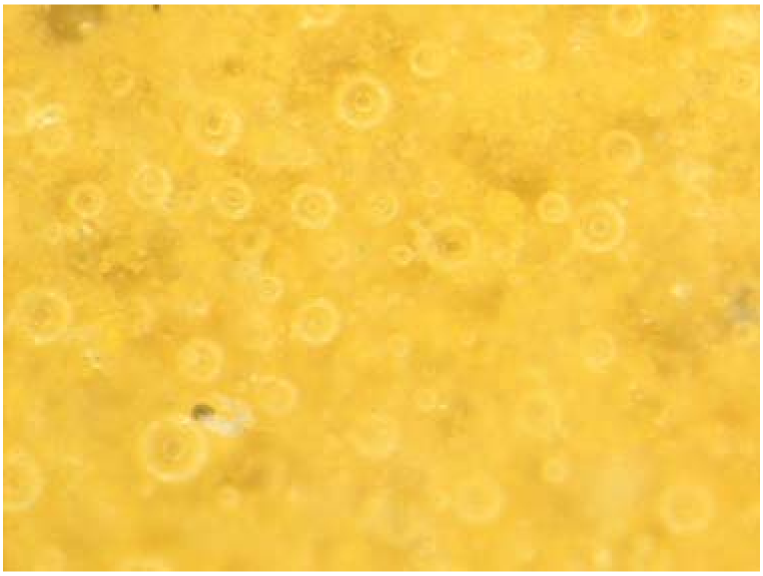

Fig.7b: Microscope enlargement 80. Hymod At in engobe with Citrus under clay color 10%wight. Test piece fired 1n the electric kiln 1200^{o}C.

Fig.8: Hymod PKH ball clay used in engobe with Citrus and Lime under clay color 5%wight and 10 %weight.

Fig.8a: Microscope enlargement 25.6. Hymod PKH in engobe with Citrus under clay color 5%wight. Test piece fired 1n the electric kiln 1200^{o}C

Fig.9: Hymod SM ball clay used in engobe with Lime under clay color 5%wight and 10 %weight.

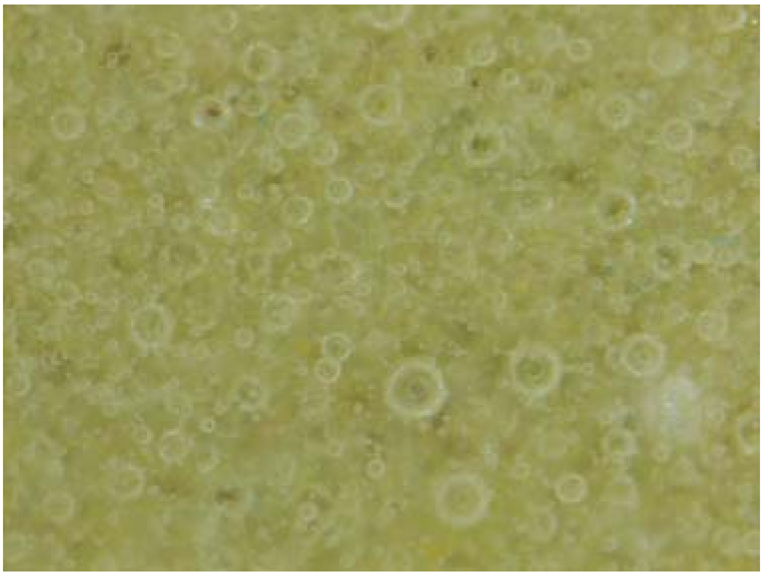

Fig.9a: Microscope enlargement 40. Hymod SM in engobe with Lime under clay color 10%wight. Lime color mixed with yellow and turquoise pigments. Test piece fired 1n the electric kiln 1200°C

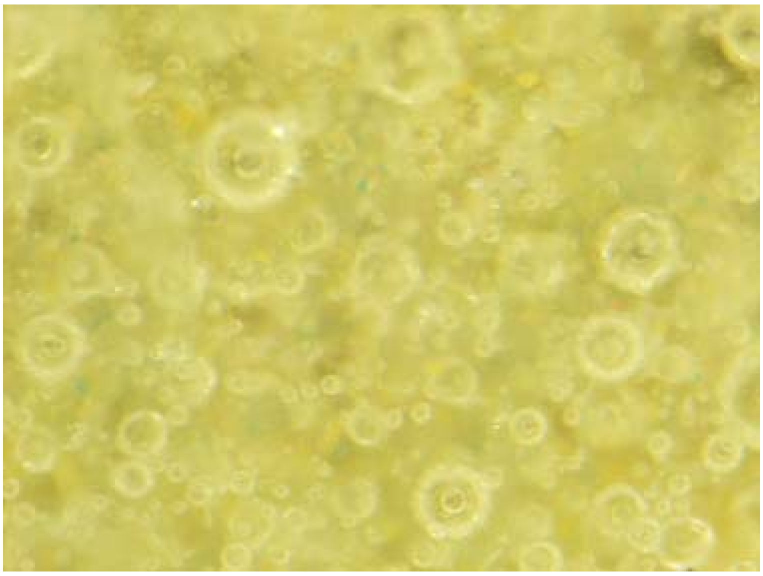

Fig.9b: Microscope enlargement 80. Hymod SM in engobe with Lime under clay color 10%wight. Lime color mixed with yellow and turquoise pigments. Test piece fired 1n the electric kiln 1200°C

4.8 Hyplas ball clays

The properties of Hyroc BKS have been compared to the Hyplas-clays. The analysis of the Hyroc BKS clay layers between the analyses of Hyplas 64 and Hyplas 71. Hyroc BKS is very suitable to be put between mass and the glaze; the amount of alkali has a sintering effect and the high aluminum oxide decreases the shrinkage. Of these clays Hyroc BKS gives the strongest coloring.

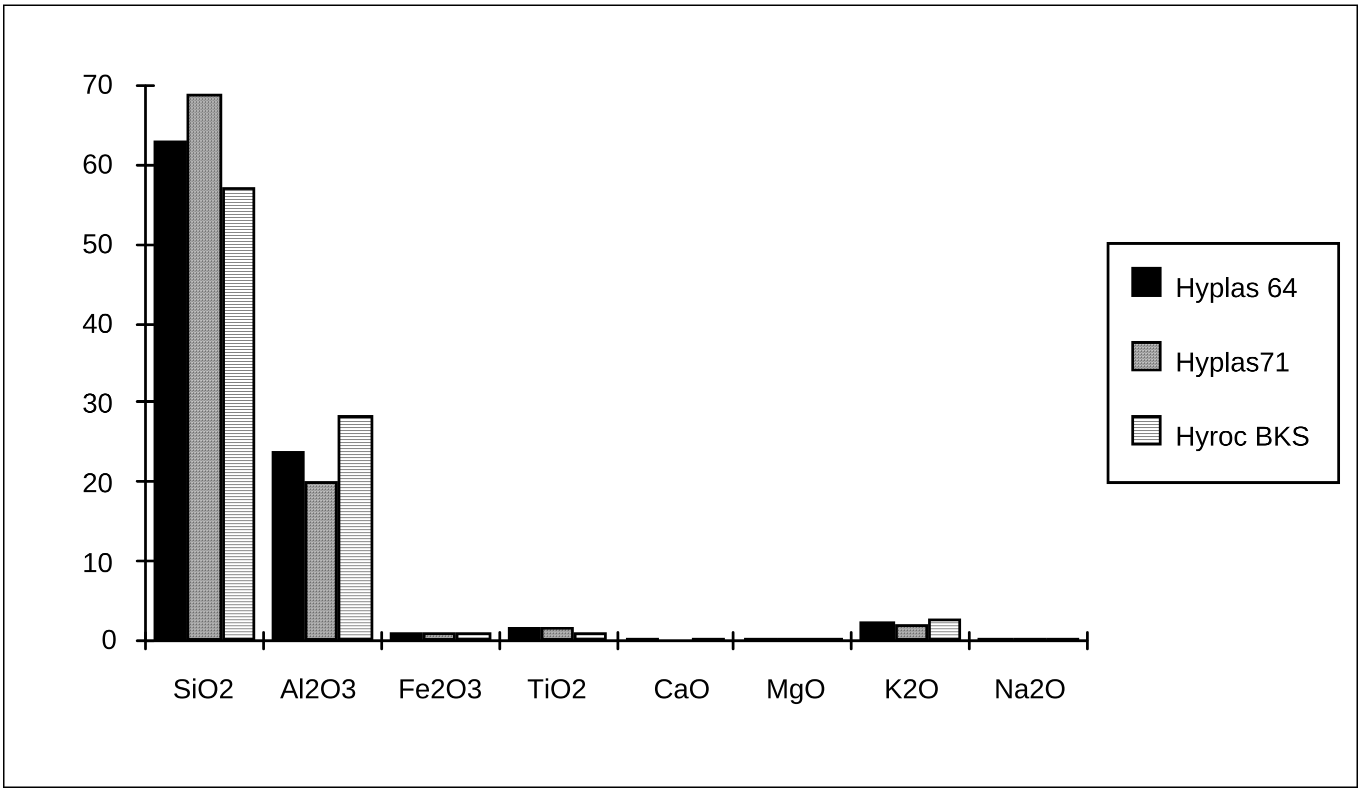

Fig.10: The oxide analyses of Hyplas 71 and 64 compared to the analysis of Hyroc BKS. Hyroc BKS differ from the Hyplas clays with respect to the high alumina concentration and also with respect to the amount of alkali.

4.9 Particle size distribution in the ball clays Hyplas 64, 71 and Hyroc BKS

When Hyroc BKS clay is compared to Hyplas 71 and 64 it is observed that the 2 ym particle size do not occur in the Hyroc BKS-clay, the particle size distribution is changed into mainly very coarse and very fine particles. BKS gives a stronger yellow color than both Hyplas clays. The shrinkage of the Hyplas clay is very suitable under the glaze, which do not crack. On Hyroc BKS the glaze cracks a bit.

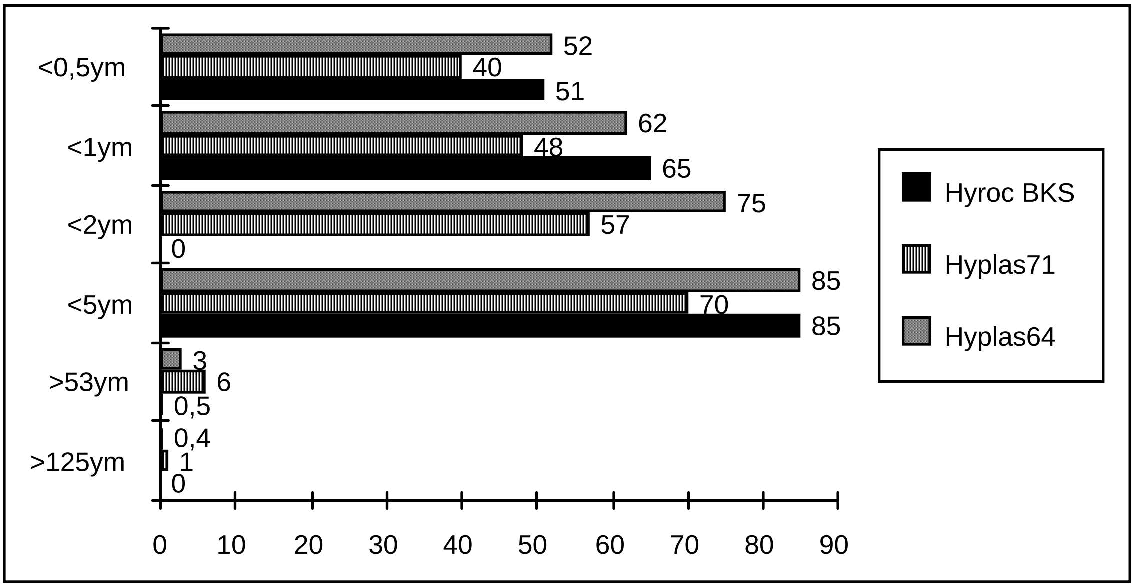

Fig.11: Comparison of the particle size distribution for the clays Hyroc BKS, Hyplas 64 and 71.

Fig. 12: Hyroc BKS in engobe with Citrus and Lime under clay color 5%wight and 10 %weight.

Fig.13: Hyplas 64 in engobe with Citrus and Lime under clay color 5%wight and 10 %weight.

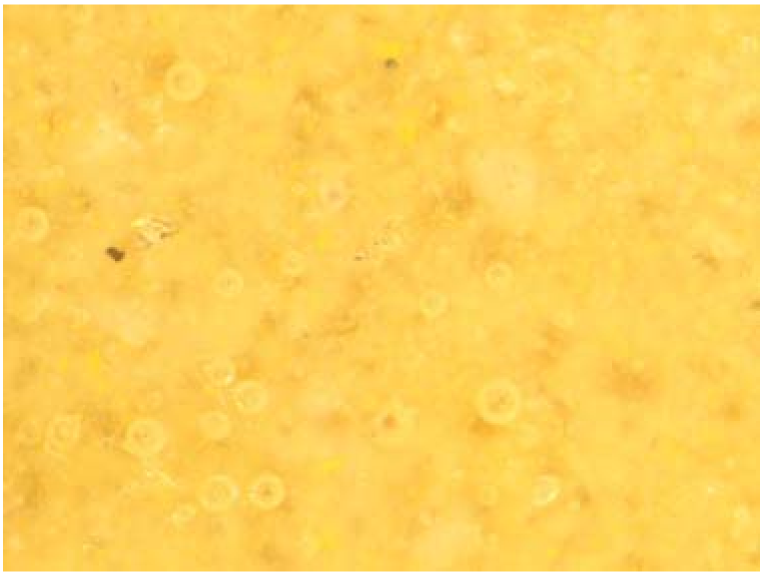

Fig.13a: Microscope enlargement 40 Hyplas 64 in engobe with Citrus under clay color 5%wight. Test piece fired 1n the electric kiln 1200^{o}C.

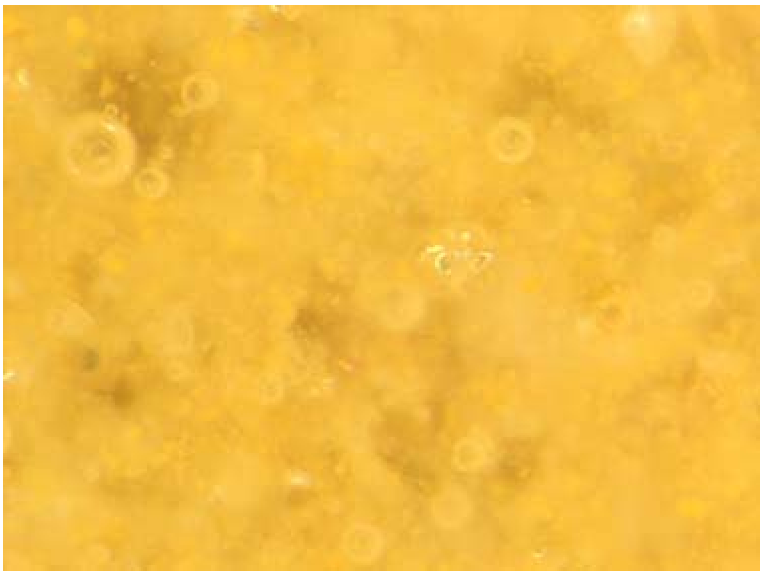

Fig.13b: Microscope enlargement 80 Hyplas 64 in engobe with Citrus under clay color 10%wight. Test piece fired 1n the electric kiln 1200^{o}C.

Fig.13c: Microscope enlargement 25.6. Hyplas 64 in engobe with Lime under clay color 5%wight. Lime color mixed with yellow and turquoise pigments. Test piece fired 1n the electric kiln 1200^{o}C.

Fig.13d: Microscope enlargement 26.6. Hyplas 64 in engobe with Lime under clay color 10%wight. Lime color mixed with yellow and turquoise pigments. Test piece fired 1n the electric kiln 1200^{o}C.

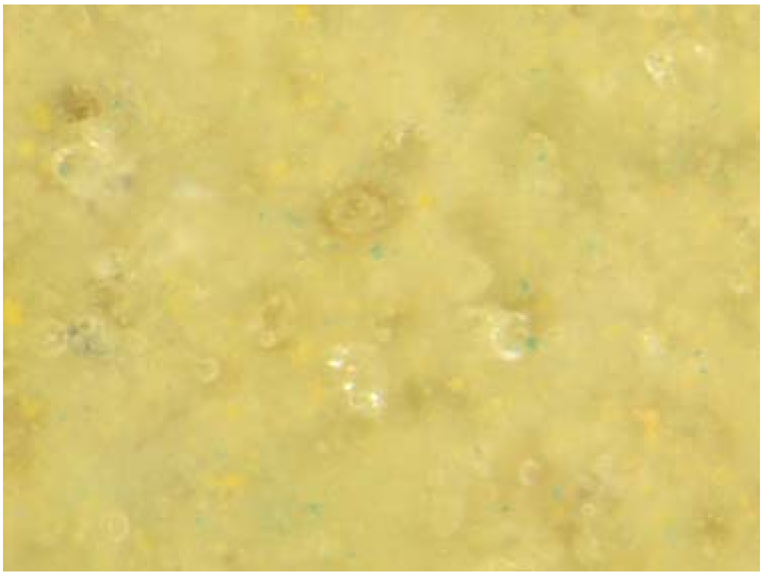

Fig.13e: Microscope enlargement 80. Hyplas 64 in engobe with Lime under clay color 5%wight. Lime color mixed with yellow and turquoise pigments. Test piece fired 1n the electric kiln 1200^{o}C.

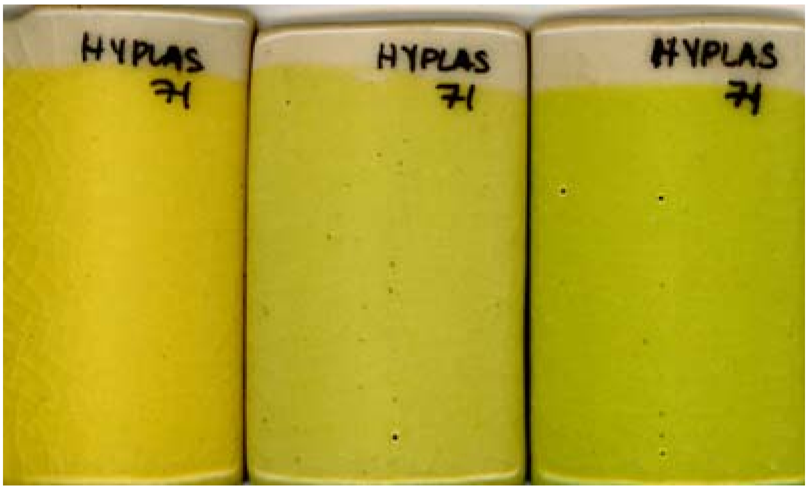

Fig.14: Hyplas 71 used in engobe with Citrus under clay color 10%weight and Lime under clay color 5%wight and 10 %weight.

Fig.14a: Microscope enlargement 25.6. Hyplas 71 in engobe with Lime under clay color 5%wight. Lime color mixed with yellow and turquoise pigments. Test piece fired in the electric kiln 1200°C.

Fig.14b: Microscope enlargement 25.6. Hyplas 71 in engobe with Lime under clay color 10%wight. Lime color mixed with yellow and turquoise pigments. Test piece fired in the electric kiln 1200°C.

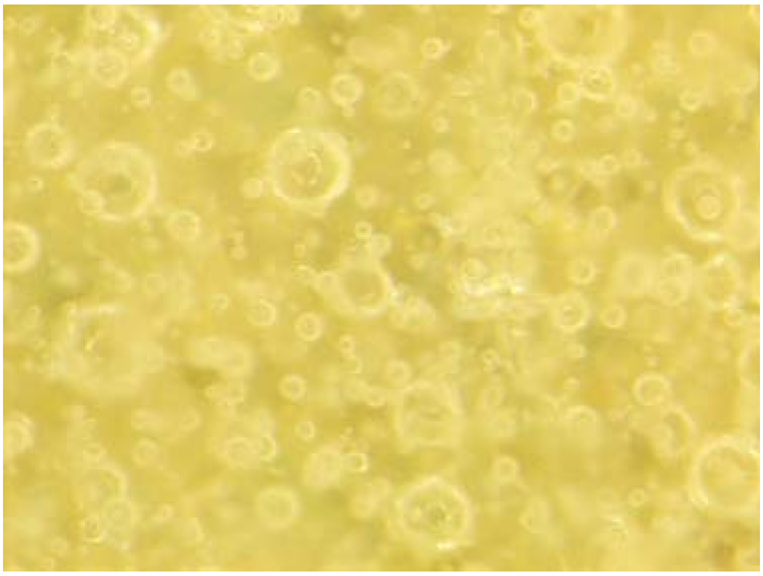

Fig.14c: Microscope enlargement 80. Hyplas 71 in engobe with Lime under clay color 5%wight. Lime color mixed with yellow and turquoise pigments. Test piece fired in the electric kiln 1200°C.

4.10 The particle size distribution of the ball clays, Hywite Alum, Hymod PKH and SM

In this picture the particle size distribution of the Hywite Alum clay, which gives a good result is compared to the particle size distribution to two clays Hymod SM and Hymod PKH, which give negative results in different ways. Hymod PKH gives a weaker color but stresses the warm yellow color, Hymod SM is distinctly more pale yellow than the just before mentioned clays. The particle size of Hymod SM clay deviates clearly by having a very cross particle size. This means in practice that the color pigment particles are not seen behind the coarse particles.

The Hywite Alum clay has a beneficial particle distribution, because it contains both coarse and fine particles, through which the glaze is able to wet the colored surface layer of the clay and form a glaze like and color reflecting bond.

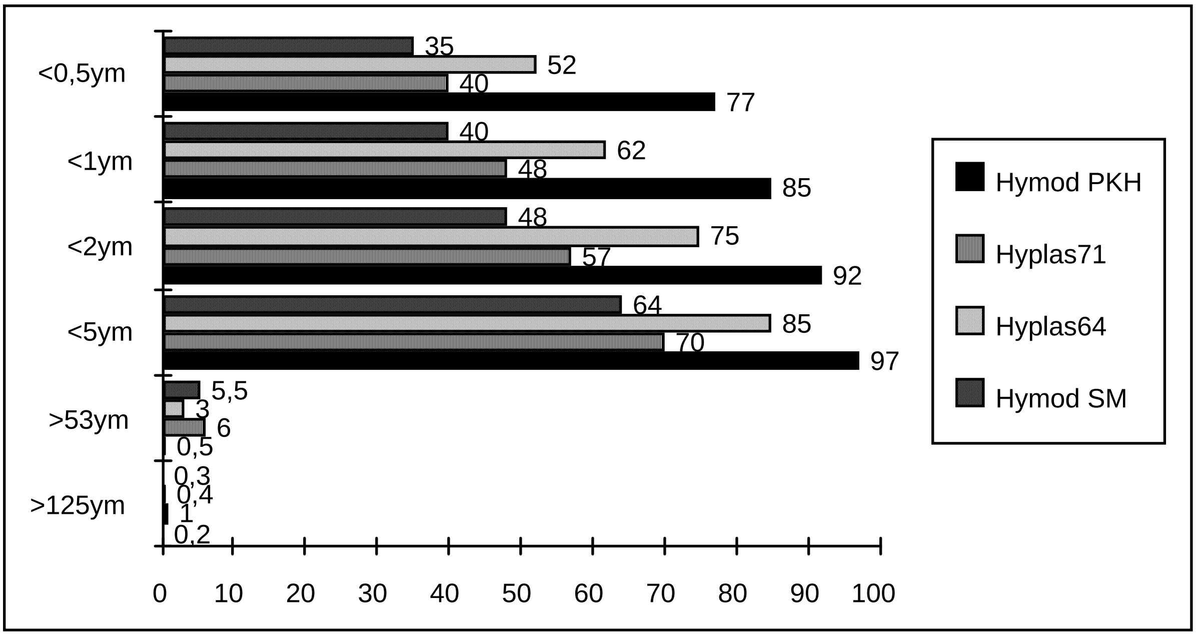

Fig.15: Comparison of the particle sizes for the Hyplas and Hymod clays. Hymod PKH has an unexceptional high amount of fine middle size particles.

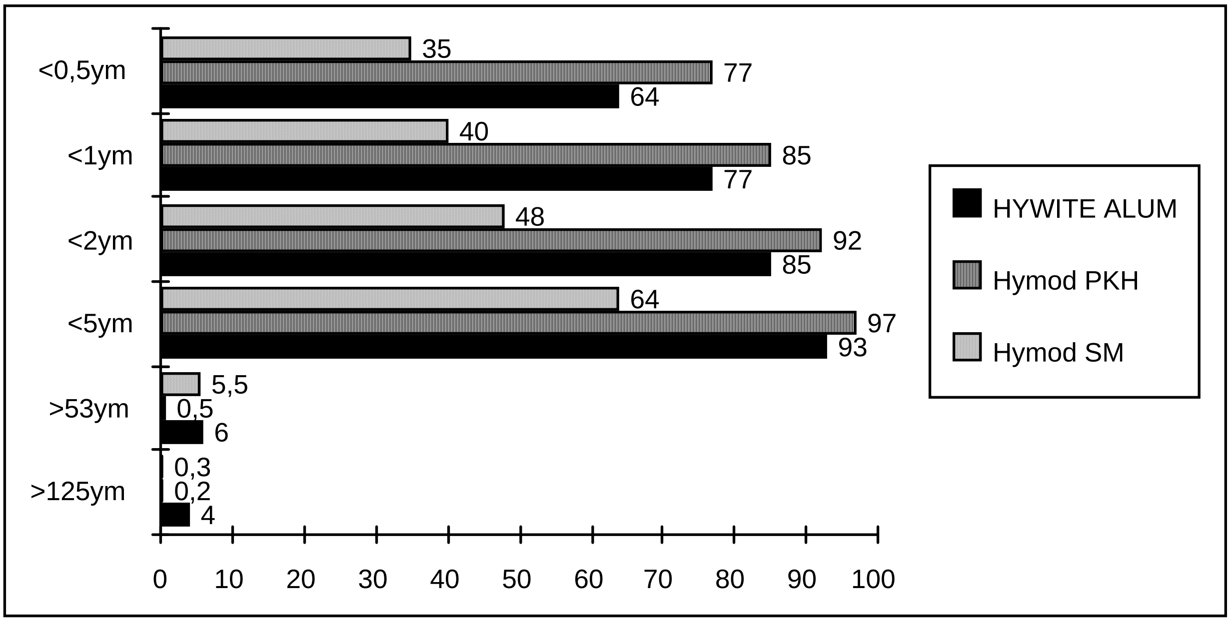

Fig.16: The comparison of the particle size distribution of the Hywite Alum, Hymod PKH and SM clays. The Hymod SM clay has crosser particle size than the Hywite Alum and Hymod SM clay is finer than Hywite Alum.

4.11 The most favorable particle size distributions of the ECC ball clays for the color pigments

The ECC ball clays Hywite Alum and Hywite Superb have the best particle-size-distributions when used with color pigments. The next best is Hyroc BKS, the particle distribution diminishes and there is a smaller amount of fine particles than in the two for mentioned. In practice the surfaces of the test pieces is coarse when a thick layer of Hyroc BKS is used.

Hymod PKH gives clearly a warm sunny yellow tone, but do not have a coloring effect comparable to the fore mentioned clays, the small particles cover the color pigment particles. The surface of the test piece is also smooth. In Figure 9 the sizes of the particles of different clays are compared. The particle size distribution of 0.5 ym - 2 ym for Hymod PKH is clearly finer than for the ball clays by which the best results have been obtained.

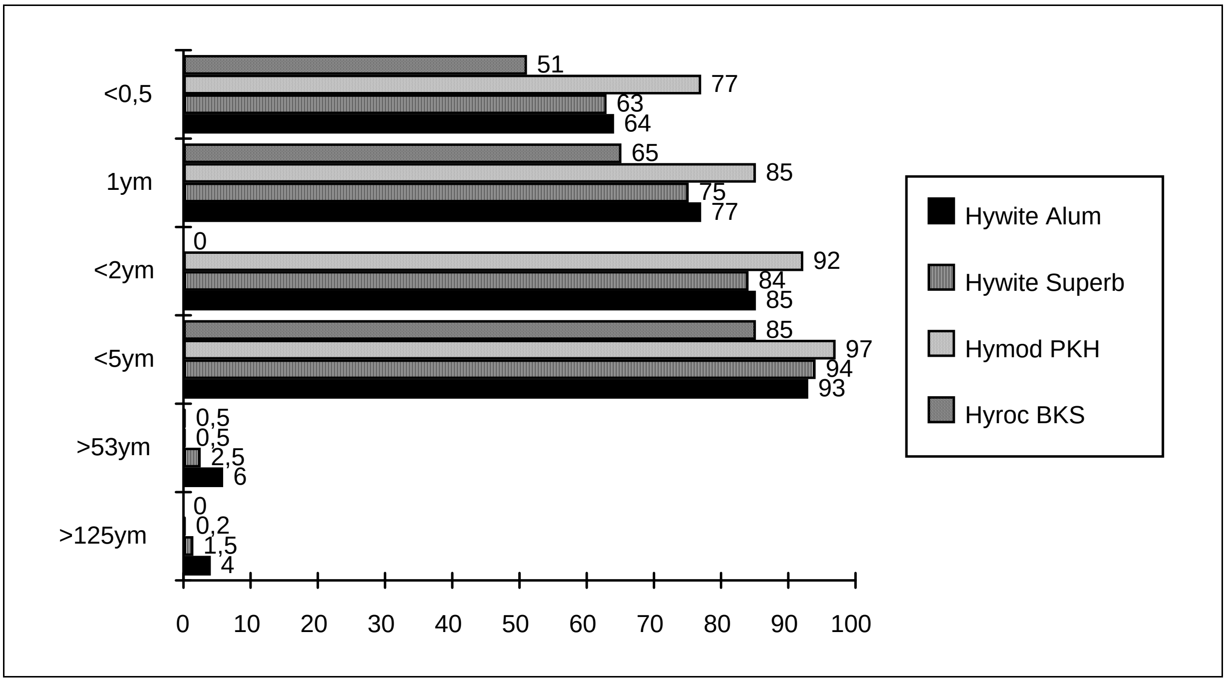

Fig.17: The comparison of the Hywite Alum-, Superb- and Hymod PKH- Hyroc BKS-clays.

Fig.18: Ball clay Hywite Alum used in engobe with Citrus and Lime under clay color 5%wight and 10 %weight.

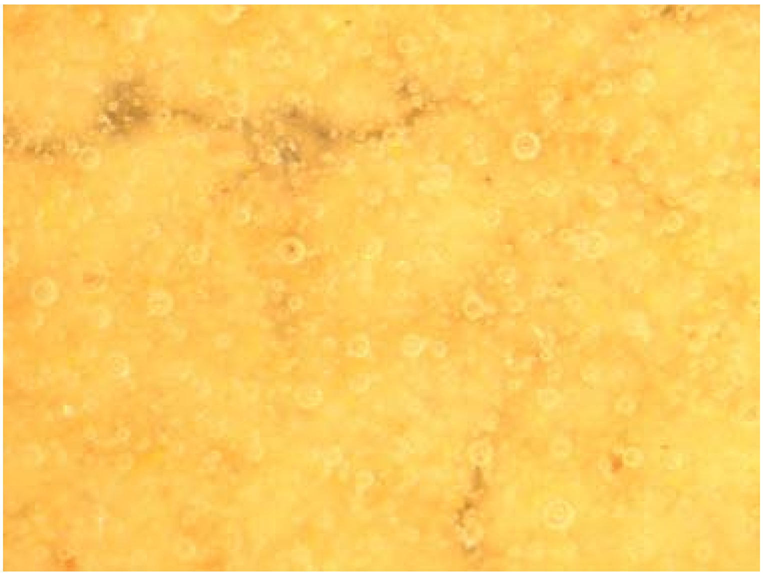

Fig.18a: Microscope enlargement 25.6. Hywite Alum in engobe with Citrus under clay color 5%wight. Test piece fired in the electric kiln 1200^{o}C.

Fig.18b: Microscope enlargement 40. Hywite Alum in engobe with Citrus under clay color 5 %wight. Test piece fired in the electric kiln 1200^oC.

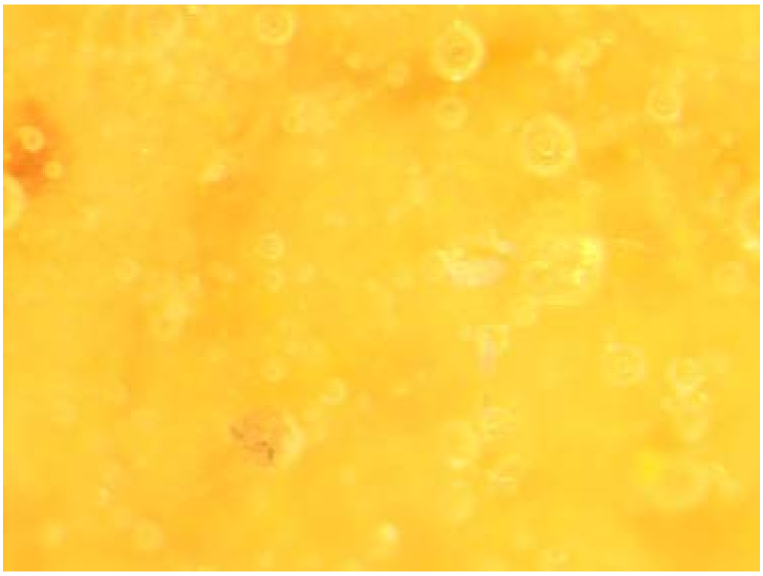

Fig.18c: Microscope enlargement 100. Hywite Alum in engobe with Citrus under clay color 10%wight. Test piece fired in the electric kiln 1200^oC.

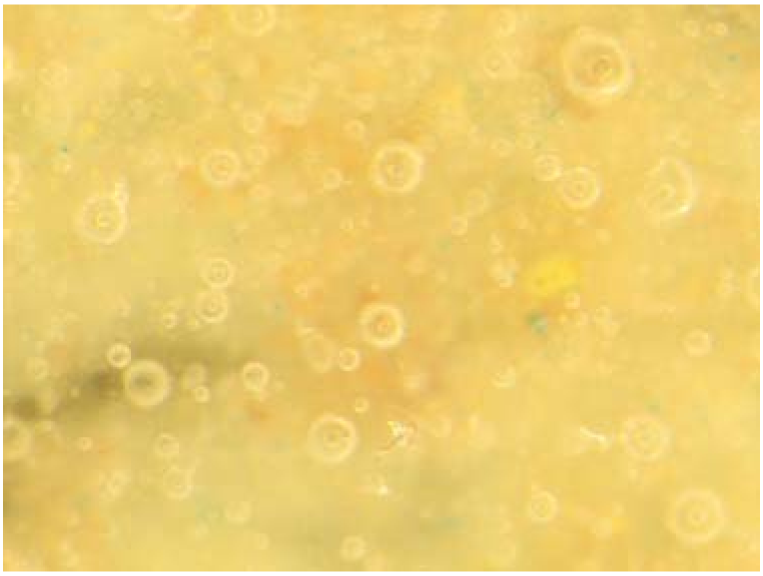

Fig.18d: Microscope enlargement 80. Hywite Alum in engobe with Lime under clay color 5%wight. Lime color mixed with yellow and turquoise pigments. Test piece fired in the electric kiln 1200^oC.

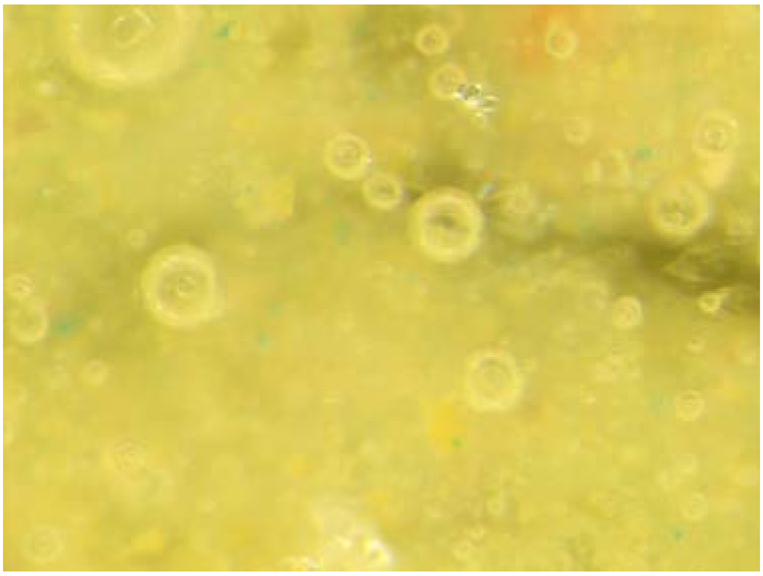

Fig.18e: Microscope enlargement 100. Hywite Alum in engobe with Lime under clay color 10%wight. Lime color mixed with yellow and turquoise pigments. Test piece fired in the electric kiln 1200^{o}C.

5 COLORS MEASURING

Measured by a color meter on a Hywite Alum test piece the result of the green color is (a-) about 6, yellow (b+) is about 38. The Hywite Superb clay test gives the value 8 for green and the value 35 for yellow. For Hyroc BKS the mean values for green is 8.5 and for yellow 32. Hyplas 64 clay has the value 9 for green and 33 for yellow. By color measurements the superiority of the clay Hywite Alum compared to other clays is clearly seen.

6 CONCLUSIONS

The coloring of the color pigments used with the different clays is directly proportional to the fact that both compounds have compatible particle distributions. Too much of a clay containing fine particles tightens the surface of the clay formulation. It is not possible for the glaze to wet the surface and the cross color particles may not be seen under the finely divided clay. Clay with a too coarse distribution covers the color pigments and thus the coloring particles are seen too less on the touching surface and the coloring weakens. The low amount of mica-minerals is directly proportional to the brightness value and at the same time also to the coloring of the pigment in the glamour of the color. The percentage of iron oxide in the clay-analysis does not, according to results from this investigation, directly affect the clearness of the color or to other changes in the color tone.