RESUMEN PONENCIA Nº 3

KAOLINITE CHARACTERIZATION TO MANUFACTURING THE CERAMIC ENAMEL

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Keys words: kaolin, ceramic, enamel, engobe.

ABSTRACT

The rise on the brasilian business at the ceramic tiles and the need of knowledge in enamels and engobes inspire this paper, the focus of this paper is the comparative characterization of Kaoliniote in the formulation of enamels and engobes. It is done reologycal initial characterization(viscosity), burn color, MEV, optical microspopy and colorimetry messures, this is done to characterization of different geological origins kaolinites., notice at this study the differences among the kaolinites at the formulations in enamels and engobes. The pegmatitics kaolins show best qualities at this formulations, and its is the well accept kaolins on the market, and the others shows differents aspects on the grain size characterization and at the physical-chemistry characterization.

OBJECTIVE

This paper has the global objective of characterization an the knowledge of the proprieties that increases the kaolin uses at the formulations at the engobes and enamels. Though , it was analise industrial supplied kaolins, that have already been comercial used , and others with different geologic origin.

The specific objective was characterization of references kaolins (have already used by industries) to subside technical and scientific the formulation of enamels and engobes. And besides analyze others kaolins that can be used at this industrial segment.

1 METHODOLOGY AND MATERIALS

1.2 VISITING THE ENAMELS AND FTITAS INDUSTRY

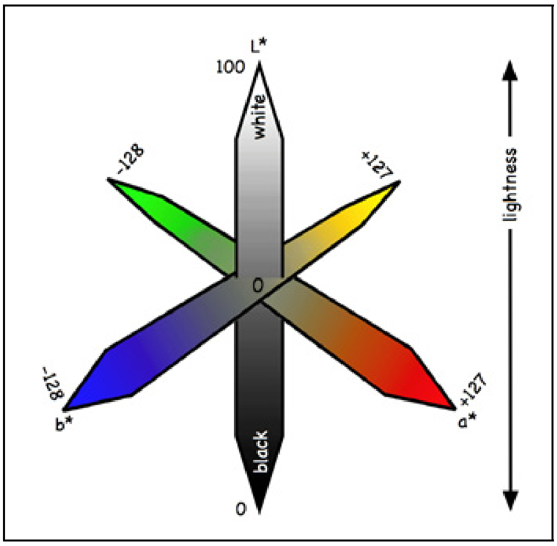
Aiming at the knowledge of the industrial process *in loco* and to obtain some kaolin are done three visits at the enamel and pigments industry , they are located near by the other tile ceramic industry localizadas. This industries are known too colorificies, produce material to the finishing of the tile, the important one are the ceramics frittas, that are made with select material, that are worned out and melted in the oven and after it is made solide by dropping in the water recipient suffering thermal shock and its stay like little fragments of glass. This material is used because its prevent the soluvel materials that can caused environmental problems and the durability of the enamel. .

1.3 KAOLIN SELECTION

The visits at Industry was need to colect some samples of kaolin and some information about the origin of this material. Besides this kaolins (four kaolins), It were added two others of the Project "Study of typology an geologiacal and technological characterization of the dposits of plastic clays and mass developing for white ceramica" (Fapesp Process 03/13762-4). This Project , is developing at the Institute of Technological Research of São Paulo (Instituto de Pesquisas Tecnológicas de São Paulo), which the author made part. And to do this selection were considered the origin and burn color of the universe of more than 30 kaolins.

1.4 LABORATORY STEP

In the laboratory there are made characterization of the diffrents kaolins with: X Ray Diffraction, sweepings microscopy (MEV), X ray fluorescence, optical microscopy, grain size analyses, reology and colorimetric assay. This laste one use the scale above..



Picture about the colorimetric classification with coordinates a*, b* e L* (COLOUR MANAGEMENT CONSULTANCY, visited in 02-07- 2007).

The formulation at this study were base on the industry formulation obtained in the visit.

The assays and some analises were done on the São Paulo State University (Universidade Estadual Paulista –UNESP- Departamento de Petrologia e Metalogenia) – Petrology and Metalogenia Department , and some are done at the Institute of Technological Research of São Paulo and in the Polithecnic Scholl (POLI)- in the University of São Paulo (USP) , some assays by the author and others by technicians.

1.5CHEMICAL ANALYZES

It is done chemical analyzes to determination of bigger and lesser oxides The methodology was the X Ray Fluorescence, that determine the bigger and lesser elements through atomic excitation , and there are Standard espectrometric samples which ones can meet with the samples of the assay .

1.6 MINERALOGICAL ANALYZES

At this step were done a Difractometer Rx analyzes and optical analyzes with the kaolinites by sinking the assay on a liquid with a known refraction index .

1.7 ANÁLISES GRANULOMÉTRICAS

The grain size analyzes were done with the Malvern method , model Mastersizer S long bed Ver. 2.19 .

1.8 CERAMIC ANALYZES

Part of kaolin samples were done some test bodies compound by 70% kaolin and 30 % albite, this was used to decrease the fire temperature of kaolin. With this bodies was done the colorimetric avaliation with the colorimeter "*Color Guide Sphere d/8º Spin*" fabrication of *Byk Gardner*, with standard observer D65 and open degree 10º.

The colors are defined by three coordinates "**L***", "**a***" e "**b***", the coordinates are orthogonal each others. The coordinate L* is brightness and darkness, letter a* is green on negative side and red on positive side, letter b* is blue on the negative side and yellow on positive side

It was done some defloculation assays to observe the reaction of the enamel with which kaolin..

2 CHOSE KAOLINS

The kaolins were chose conform burn color and how its occur at the nature(diferents geologicals origins). The standard samples of kaolin are shown at the table one and the others that were chose on the table two.

Table 1: Standard samples

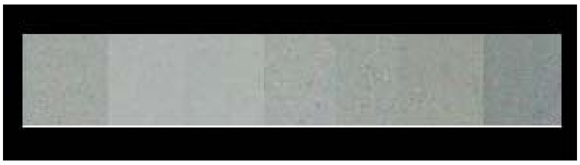
Standard Samples	Amostras	Geology
	DA 151	Pegmatite kaolin
	DA153	Pegmatite kaolin
	DA 154	Granite Kaolin
	DA ESM	Pegmatite kaolin

Table 2: The exploratory samples:

Exploratory samples	Selection base don:: Different geological origin mIneralogical characteristics e Grain Sizes Burn color	RS-47-Mariana Pimentel- mudstone of Paraná Basin
		RS49- Pântano Grande – Kaolin Anorthosite Capivarita

Below some clays that were chose by color burned:

brightness Clays
32 - A-Apiaí P04
47- Mariana Pimentel
36 - Alto Tietê
49 - Pantano Grande
42- Campo Largo
18 - São Simão
44 - Campo Alegre



Picture 1 : Picture with some bright select clays.

3 DATA BY INDUSTRIALS FORMULATIONS OF ENAMELS AND ENGOBES

Table 3: Formulation of engobe

Engobe	Porcentagem	Massa(g)
White Fritta	30%	90g
Kaolin	20%	60g
São Simão Clay	10%	30g
Feldspar	15%	45g
Quartz	20%	60g
Zircon	2,5%	7,5g
Talc	2,5%	7,5g

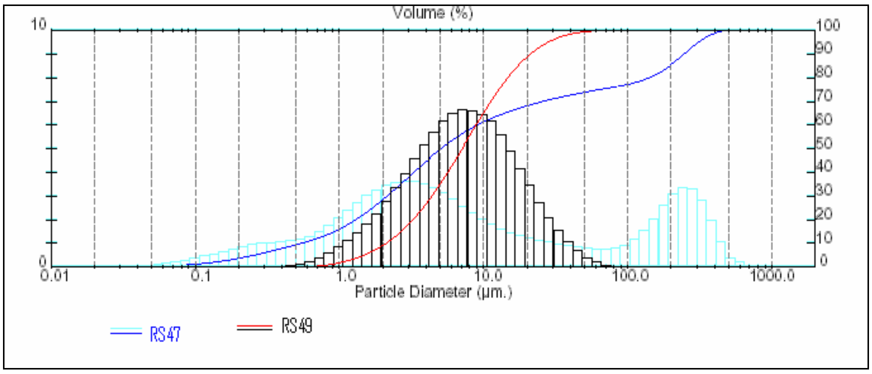
Table 4: Formulation of transparent enamels

Esmalte	Porcentagem %	Massa
Transparent fritta	80%	240g
Kaolin	5%	15g
Albite	10%	30g
Quartz	4,7%	14,1
CMC	0,3%	0,9
TPF	0.85g/100ml H_2O	

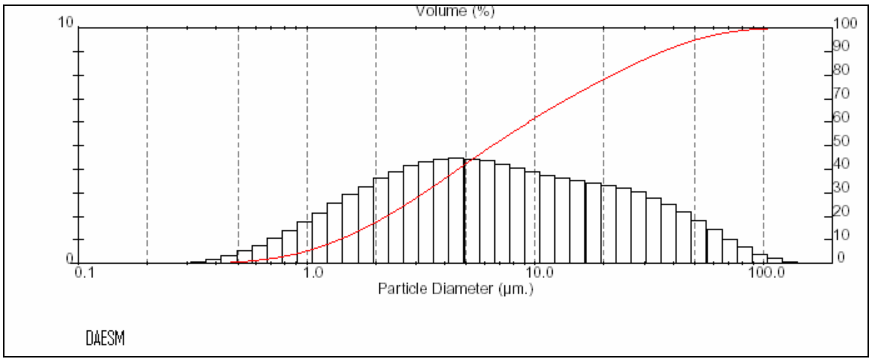
4 GRAIN SIZE

One of the great parameter to know the technological reaction of the ceramic material is its grain sizes distribuition, its interfer in the reology , plastic fenomenal, green and burn hardness,

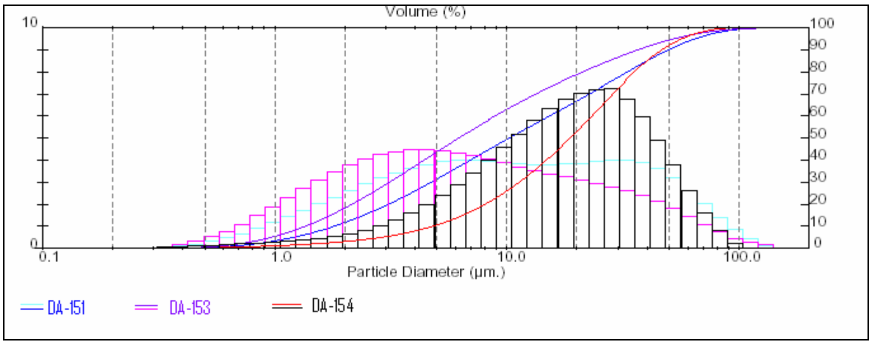
On histogramas at the pictures 2, 3 e 4 observe the similar grain size distribution of the pegmatitics kaolins (151, ESM, 153) the distribution are around by 1,0 to 100,0µm, and uniform, althoug the distribution in kaolin RS49(anorthosite one) is little dispersive , its charater should be because the great concentration in the origin rock with anorthita(90% of the rock). And the kaolin 154 shows the concentration of the grains on 10 until 100µm, with an assimetric histogram (até 100µm). The kaolin RS 49 shows two picks, its reflects its chemical composition with great quantities of quartz (100 e 1000µm), its origin is the sediments of Rio do Sul Formation, its reflects great variation of its sediments.



Picture 2: Grain size distribution kaolins RS 47 e RS 49



Picture 3: Grain size distribution Kaolin ESM.



Picture 4: Grain size distribution 151, 153 e 154

5 CHEMICAL ANALIZES

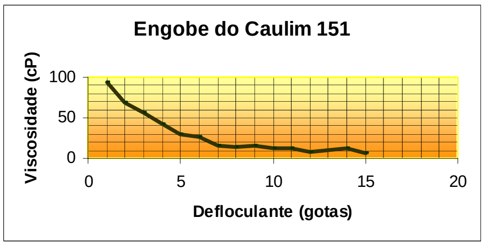
Table 5: Chemical kaolin analizes

labogeo	amostra	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	LOI	Soma
DAM9545	DMC-151	47,81	0,00	37,00	0,36	0,01	0,21	0,04	0,39	1,11	0,16	12,92	100,01
DAM9546	DMC-153	47,50	0,01	37,23	0,47	0,01	0,17	0,06	0,21	0,76	0,12	13,47	100,00
DAM9547	DMC-154	46,51	0,08	37,62	1,07	0,03	0,24	0,02	0,20	1,24	0,06	12,95	100,01
DAM9548	D ESM	47,34	0,02	37,51	0,48	0,01	0,20	0,05	0,29	0,76	0,07	13,27	100,01
MOTTA9240	RS-47	80,37	0,57	13,6	0,17	0,01	0,03	0,03	0,06	0,22	0,04	4,94	100,04
MOTTA9241	RS-49	50,33	0,11	32,96	0,72	0,01	1,46	0,51	0,07	1,31	0	12,56	100,03

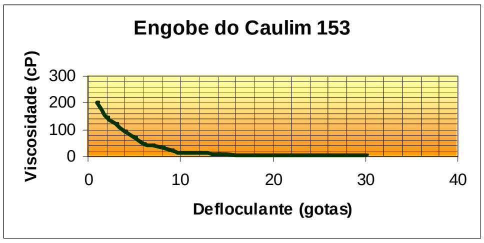
6 REOLOGY

Curves of defloculation with sodic tripoliphosphate TPF 0,85%.The suspension was made for engobes with 300ml water for 300g blended material and for enamels 250ml water for 300g blended material, these were made for all the kaolins, and it´s done because the pratical methodology to take the material inside the blended mill with porcelain balls.

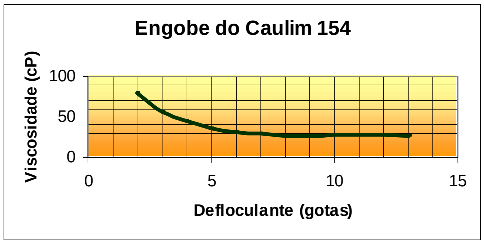
Defloculation curves of enamels Table 3 (engobes) e Table 4(enamels):



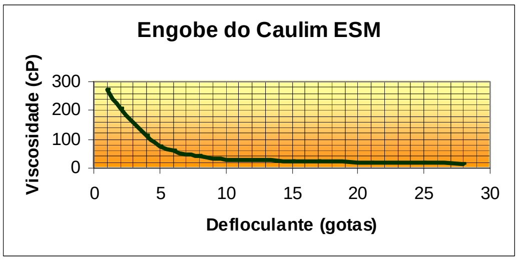
Picture 5: Defloculation curve 151.



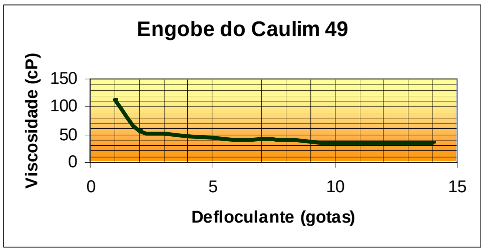
Picture 6: Defloculation curve 153.



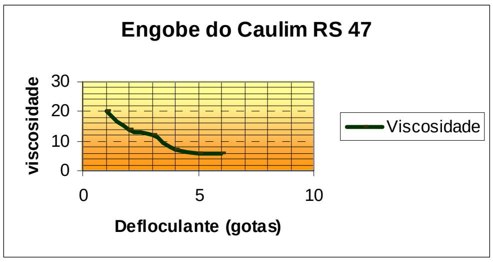
Picture 7: Defloculation curve 154



Picture 8: Defloculation curve ESM.



Picture 9: Defloculation curve 49.

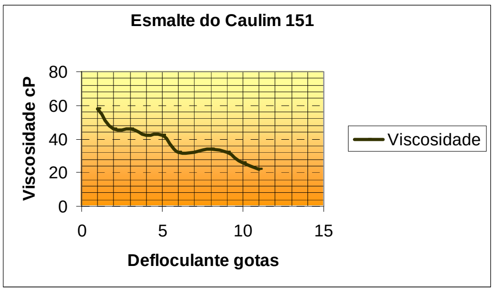


Picture 10: Defloculation curve

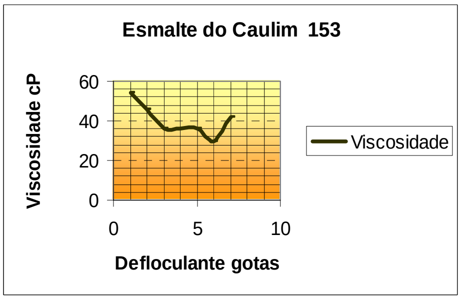
How we could observed at the previous graphics kaolins 151 and 154 reached na assintotic in the defloculation curve with five drops of defloculat, besides kaolins ESM, while kaolin RS49 reached na assintotic with less than three drops. And the kaolim 153 reached an assintotic with ten drops of defloculant .

Here follow the enamels viscosit curves (Pictures 16 a 21) .Some enamels the viscosit drop down and with the increase of defloculant liquid reach na critical point and it increase then drop down again and do not reach na assintotic as like in the engobes.

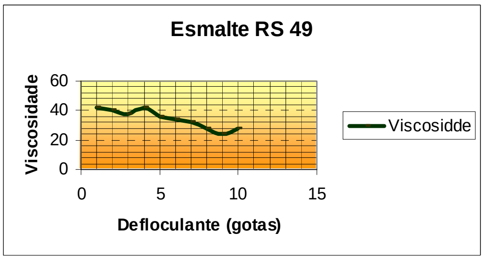
Bellow follow the viscosit curves:



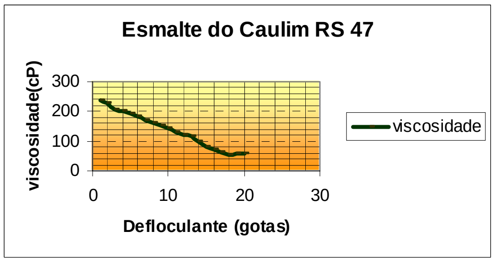
Picture 11: Deflocculation Curve of enamel 151



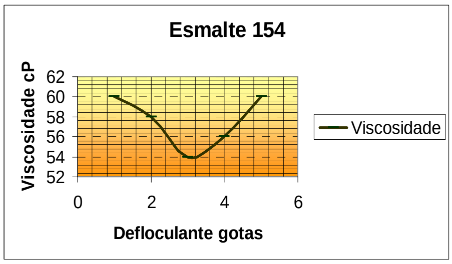
Picture 12: Deflocculation Curve of enamel 153



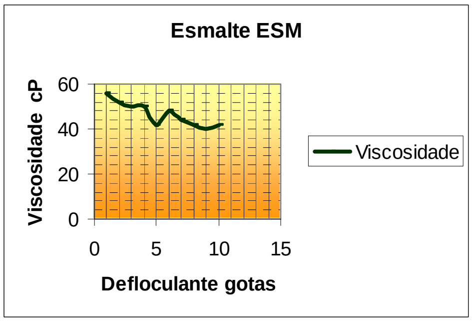
Picture 13: Deflocculation Curve of enamel RS 49



Picture 14: Deflocculation Curve of enamel RS 47



Picture 15: Deflocculation Curve of enamel 154



Picture 16: Deflocculation Curve of enamel ESM.

O caulim RS 47 primeiramente foi utilizado integralmente na formulação mas apresentou problemas ao se elaborar a formulação de engobe, assim foi necessário passar por peneira malha 200 para separar os grão de quartzo, os quais pela análise química compões cerca de 80 % da amostra.

7 COLORIMETRY

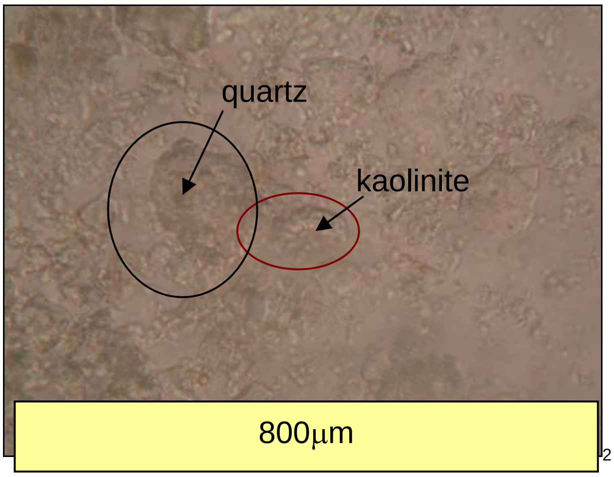
The colorimetric assay shows that the pegmatitic kaolins are whiter than the others.

Table6: Colorimetric assay, results.

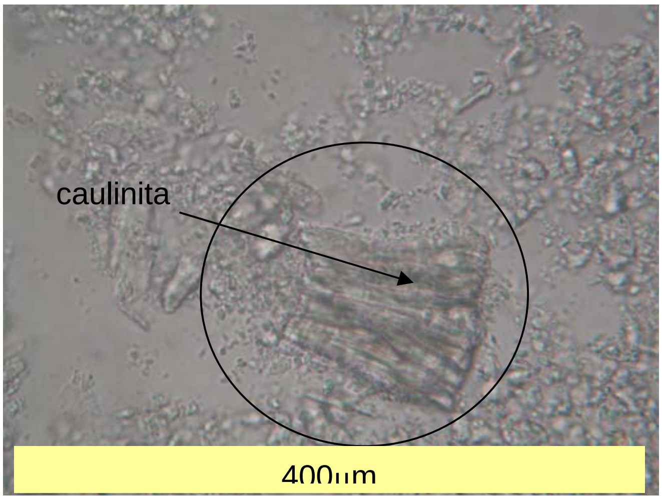
Colorimetry				
151	Test body	L*	a*	b*
	1	94,38	0,8	4,01
	2	94,4	0,8	4,12
	average	94,39	0,8	4,07
153	Test body	L*	a*	b*
	1	95,04	0,68	4,42
	2	93,72	0,69	4,52
	average	94,38	0,69	4,47
154	Test body	L*	a*	b*
	1	90,23	1,53	5,1
	2	90,25	1,53	5,18
	average	90,24	1,53	5,14
ESM	Test body	L*	a*	b*
	1	94,78	0,5	4,08
	2	94,89	0,48	4,21
	average	94,83	0,49	4,15
RS 47	Test body	L*	a*	b*
	1	92,29	1,15	5,32
	2	91,15	1,07	5,28
	average	91,72	1,11	5,3
RS49	Test body	L*	a*	b*
	1	89,88	1,37	8,35
	2	89,5	1,34	8,46
	average	89,69	1,36	8,4

8 OPTICAL MICROSCOPY

Micrograph of kaolin RS 47 (Mariana Pimentel) shows lots of quartz grain(it can be observed at the chemical analyzes), this quantities of quartz caused bad blended enamel then it must to separated the bigger grains (# 200) to best performace on defloculatin an blendation .



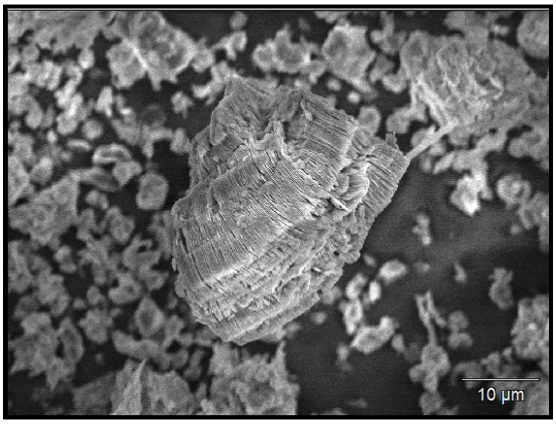
Picture 17: Caulim 47 – Kaolinite grain and quartz grain optical microscopy 40X objetiva - 10X ocular.



Picture 18: Leves of kaolinite by optical microscopy

9 SWEEPING ELETRONIC MICROSCOPY (MEV)

At this view of sweepings microscopy (MEV) can be observed sheets of kaolinite..



Picture 19: View of sweepings microscopy (MEV) kaolin 151

10 CONCLUSIONS

The kaolins must be on ideal conditions of purityness, grain size, colorimetry aspects, mineralogical compositions. The pegmatites ones are more bright and have an peculiar distribution of the grain size. The viscosity vary with the kaolin. The viscosities of the kaolins in the enamels formulations decrease and reach a critic point then raise up. While the viscosity of the engobes reach an assintotic curve. The kaolinite RS 47 must be classified on grain size because it has a lot of SiO_2, how it´s observed in the chemical analyzes. Some formulation with alumina was done but its viscosity became high because this alumina was micronizide. The kaolin 154 shows a great rise of the viscosity it can be because the composition with Iron, this is not too bright, it shows a kind of rose color observed by eyes.

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