Improving Hiding Power Obtained by Variation of Fillers for Interior Emulsion Paints

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This paper presents a study who emphasizes the importance of the choice of fillers and together with a performance quality of white pigment to help achieve those desired for interior emulsion paint. Thus, we studied various types of fillers (sulfates, silicates, calcium carbonate) with white pigments (zinc oxide, titanium dioxide) in a copolymer of ethylene vinyl acetate (EVA) and all these combinations analyzed and measured by values of hiding power, white and yellow index.

Keywords: coating emulsion, fillers, white pigments, interior emulsion paints

To obtain a quality and stable paint is necessary to establish the optimal technological parameters. Although, the basic principles can be found in the literature of World War period when Schou describes the possibility of obtaining emulsified paint binders based on triglycerides, emulsified paints are relatively new [1]. An emulsified paint systems development occurred only after the Second World War, when become available quantities of butadiene and styrene plants manufacturing synthetic rubber. These materials combined to form butadiene-styrene latex, became able to make paint diluted with water. There are today three main types of latex used as binders for paints, namely: styrene-butadiene copolymers, poly-vinyl-acetate and acrylic polymers and copolymers. The term of latex based paint was given initially to emulsified styrene-butadiene paints, but now it defines all polymer systems made with emulsified [2-3]. Close correlation that exists between the rheological behavior of a system and the structure of some non-newtonian mixture was analyzed and explained in many works, showing its importance and its influence on other elements of the system [4].

Materials and devices

The Base – it was used a base that includes the main components of paint: copolymer and ethylene vinyl acetate (EVA), cellulose-ether thickener, filler, preservative (biocide), water and ammonia solution. The Base's characteristics are presented in table 1.

Water based paint is a nano dispersion of a solid component called Base and fillers in an aqueous medium [5]. To give a stability and other properties than hiding power, white and yellow index it is need to add foaming agent, dispersing agent, coalescent agent and fillers. The fillers used were: natural calcium carbonate (CCN), precipitated calcium carbonate (PCC), titanium dioxide, opaque polymers, sodium aluminum silicate, 14.5 SiO_2 * 1.4 Na_2O * Al_2O_3, mica, talc, kaolin, micronized barite, diatomite, $BaSO_4$, silica. Optical properties of pigments and fillers are determined by the refractive index difference between air and pigment or filler. The higher the diference the bigger the hiding power [6]. The substances with a refractive index higher than 1.7 are generally called white pigments. Bigger differences occur between air and fillers with the effect that everywhere there is an interface between pigment and air or between filler and air there is a distinct increase of hiding power. All raw materials used in this study were chosen so as to meet European Union legislation on the environment [7].

It assumes that the original recipe has 60% in weight fillers. This percentage will be distributed to each type of fillers depending on the composition, role and its ratio relative to the resin from Base.

Experimental part

Besides the Base, a water based paint requires also other components(table 2).

No.	Characteristics	Average value	Test Method
1	Density at 25 ^{0}C, g/cm^3	1.04	SR EN ISO 2811-1:2002 SR EN 932-5
2	Solid content, %	20	DIN EN ISO 3251; 4h; 105^{0}C
3	pH at 25 ^{0}C	9	DIN ISO 976
4	Brookfield Viscosity R6; 5 rpm la 25 ^{0}C, cP	40000	DIN EN ISO 2555; rotor 5; 2.5 rpm, 23^0 C
5	Resin content in wet, %	15	SR ISO 247:1995
6	Resin content in dry, %	75.5	SR ISO 247:1995
7	Organic content in wet, %	2.5	SR ISO 247:1995
8	Organic content in dry, %	11.5	SR ISO 247:1995

Table 1
CHARACTERISTICS OF USED BASE

Nr. Crt.	Raw material	Composition, %
1	**The Base**	30
2	Antifoaming agent – Mineral Oil	0.2
3	Dispersing agnet – Sodium polyacrylate	0.3
4	Co-alescent agent - Butyldiglycol	1
5	Water	8.5
6	Fillers (TiO_2, opaque polymer, sodium aluminum silicate, micronized barite, mica)	60
	TOTAL	**100**

Table 2
COMPONENTS OF WATER BASED PAINT

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No.	Raw material	Composition / variants of paints											
		V 1	V 2	V 3	V 4	V 5	V 6	V 7	V 8	V 9	V 10	V 11	V 12
1.	Water	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5
2.	CCN 2 µm	30	25	22.5	23	22.5	22.5	22.5	20.5	22.5	22.5	22.5	22.5
3.	CCN 5 µm	30	25	22.5	23	22.5	22.5	22.5	20.5	22.5	22.5	22.5	22.5
4.	Titanium dioxide	0	10	10	6	7.5	10	10	6	11	7.5	7.5	5
5.	Zinc exide	0	0	0	0	0	5	0	0	0	0	0	0
6.	Talc	0	0	5	0	5	0	0	5	0	5	5	5
7.	CCP	0	0	0	8	0	0	0	8	0	0	0	0
8.	Sodium aluminum silicate	0	0	0	0	2.5	0	0	0	0	0	0	0
9.	Caolin	0	0	0	0	0	0	0	0	0	2.5	0	0
10.	China clay	0	0	0	0	0	0	0	0	0	0	2.5	0
11.	Micronized barite	0	0	0	0	0	0	5	0	0	0	0	0
12.	Mica 40	0	0	0	0	0	0	0	0	4	0	0	0
13.	Opaque polymer	0	0	0	0	0	0	0	0	0	0	0	5

Table 3
VARIANTS OF PAINTS

The variants underlying of this study are presented in table 3.

There have been twelve versions of compositions of paints so that after tests carried out to define the influence of those components and their concentrations on opacity, white index and yellow index.

The quantities of fillers were based on data sheets that recommended optimum dosage for each filler in the formula.

These are theoretical formulations as a starting point for a further study. Each variant can be analyzed separately and represents a small-scale study. There are not final formulations but only alternatives to be further developed and analyzed.

Main equipment

A Byk Gardner Spectrophotometer for measurements dried paints films: Contrast Ratio (Opacity, Hiding Power), White Index and Yellow Index, Reflectance Index was used.

There have been also used the following devices: Bar-Type applicator, Opacity Drawdown Charts, Brookfield Viscometer - measuring viscosity by sensing the torque required to rotate a spindle at constant speed while immersed in fluid, the torque is proportional to the viscous drag on the spindle, thus with the sample viscosity; Cup Volume; Oven at 105°C; electronic pH meter; Oven heated at 950°C; the Fineness of Grind Gage used to indicate the fineness of grind or the presence of coarse particles or agglomerates in a dispersion and a Pfund Cryptometer which determines the wet hiding power of a coating within a few minutes.

Procedure

To obtain an interior latex paint similar with the one that meets the market requirements, called Standard (S), there are proposed to be prepared using a simple laboratory dissolvers - Dispermat, twelve variants, a minimum amount of 1.5 kg for each variant, with the same errors in weighing (same electronic scale), the same batches of raw materials are kept constant, the same technology and policy input materials while mixing and the same operator. The variants obtained are stored in the same conditions of temperature and humidity in the laboratory (20 + / - 30° C, 50%), and analyzed after 24 h of preparation. The analysis of these variants will be made by the same operator in the same working conditions to eliminate as many errors as possible.

The technological process is: the Base, half quantity of water, coalescent agent, half of antifoaming agent and dispersing agent, are mixed at medium speed of 400-500 rpm for 5 min, then add the fillers, using a high speed of 1000-1200 rpm, and the rest of water, allow to mix for 1-2 h, until a fine paste is obtained (50 µm using Fineness of Grind Gage), apply a thin layer on a glass plate to see the dispersion of the film, then reduce speed to 300-400 rpm, and add the difference of antifoaming agent, and left to a slow speed for 2 min.

Results and discussions

Paints formulations V1-V12 in liquid form were analyzed in terms of viscosity, density, content of volatile, resin content and organics, fineness, *p*H and hiding power measured as the specific consumption.

Table 4 contains the characteristics of these liquid formulations.

The physico-chemical characterization of the Standard (S) sample with the rest of the variants obtained is shown in table 4.

As content of the resin, all the twelve variants analyzed are clearly superior to Standard reference paint,

Table 4
PHYSICO-CHEMICAL CHARACTERIZATION FOR ALL VARIANTS

No	Characteristics	S	Values / Variant											
			V 1	V 2	V 3	V 4	V 5	V 6	V 7	V 8	V 9	V 10	V 11	V 12
1.	Brookfield Viscosity, R5; 2.5 rpm	25120	65600	64000	60800	72000	70400	104000	75200	68800	80000	92800	76800	57600
2.	Density, g/cm³	1.6191	1.585	1.670	1.670	1.672	1.659	1.737	1.741	1.675	1.561	1.715	1.708	1.606
3.	Solid content, %	61.55	67.96	68.74	67.91	68.61	68.24	70.55	70.04	69.73	68.68	71.49	70.95	66.17
4.	Resin content, % Wet Dry	2.34 3.80	6.78 9.97	5.96 8.67	6.48 9.54	5.54 8.08	6.56 9.62	4.85 6.88	6.15 8.78	5.44 7.80	5.08 7.39	6.47 9.05	4.47 6.31	7.22 10.91
5.	Organic content, % Wet Dry	35.09 57.02	33.96 49.97	39.97 58.14	40.75 60.00	38.22 55.72	40.90 59.94	43.47 61.62	43.24 61.73	40.92 58.69	42.13 61.35	43.58 60.93	43.48 61.28	36.45 55.08
6.	Fineness, µm	60	50	30	35	35	30	30-35	40	30	-	35	35	20
7.	Hiding power, l/m²	3.96	2.38	4.75	4.40	4.75	4.75	5.94	5.40	4.75	3.83	4.10	3.96	4.75
8.	pH	9.01	8.79	8.83	8.79	8.87	8.94	9.55	9	9.11	9.17	9.10	9.18	9.24

demonstrating that this paint film will have a better adhesion to the substrate and also a high wet scrub resistance. The difference of viscosity between Standard and studied variants can be adjusted by adding water, which will leaded to a decrease in resin content and implicit a less hiding power. A triple value of viscosity does not bother with anything, it can be reduced by adding water to the application so to have a good application, without suffering major differences in other characteristics. The fineness, the dispersion of fillers, have an important role in the formulation of paints, leading to a homogenization as good as possible, close to that of a paste, with a good hiding power but also the adequate chemical stability. The fineness should be max. 50 μm, the smaller. the better

The hiding power measured as the specific consumption, increases with the variation of fillers in formula, their lack from formula very clearly being shown (eg V1), but not always a better hiding power lead to acceptance like a final version. It must be relevant with other characteristics such as density, fineness, solid content.

A *p*H between 8 and 9 lead to a safe stability for paint, and avoid the formation of bacteria and fungi that develop in aqueous medium at a *p*H below 8.

In conclusion, from all twelve variants studied and analyzed, just V2, V5, V6, V8 and V12 may be taken as variants to be used for another tests.

Characterization of dry paint film applied on Opacity Drawdown Charts

The only meaningful way to compare two different batches of paint is to have a dry film of uniform thickness and texture. Bar-Type applicators with which we applied wet film of 75 microns are used to determine hide or contrast ratio. To measure the accurately of color and gloss we can apply 100 microns (or higher).

Each variant studied, including the reference one - Standard, were applied after 24 h of manufacture, on the Test Chart, using a Bar Type applicator with 75 microns, let to dry and compared visually but also graphically analyzed.

All readings are according to the standards of the International Commission for Lighting (CIE). In practice light sources are:

- daylight, D65, C;
- the incandescent light
- fluorescent light F2, F11.

Contrast Ratio (Opacity, Hiding Power) variation – presented in figure 1

Essential sales criteria for architectural paint are hiding power and yield. In other words: how many layers are necessary for the complete coverage and how many cans will be needed?

Opacity is a measure for hiding power:

$$\text{Opacity}(\%) = \frac{\text{YBLACK}}{\text{YWHITE}} \times 100\ (\%) \qquad (1)$$

Where: YBLACK = the value measured on black area on the chart;
YWHITE = the value measured on white area on the chart.

100% opacity means complete hiding, no differences can be seen between the drawdown on black or on white.

Procedure

A uniform paint film is applied on a black / white contrast chart. After air drying the drawdown can be objectively evaluated using the BYK-Gardner spectro-guide. The operator is menu guided through the measurement procedure and the opacity value is automatically displayed [8-9].

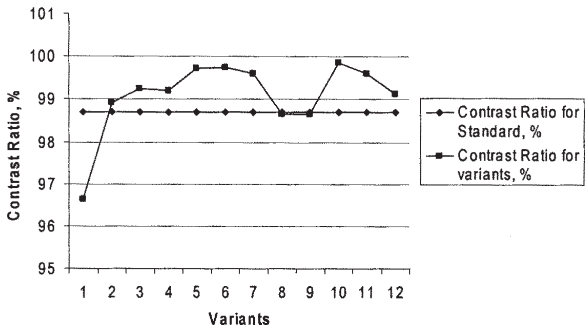

Fig. 1. Contrast Ratio variation

The contrast ratio value for Standard reference sample is not a very big , 98.71%, nine of the twelve variants having higher contrast ratio values than this one, but this characteristic needs to be correlated with the rest of characteristics, like White Index, Yellow Index, so from all these nine variants only V5 variant has this condition and has 99.72% like contrast ratio value.

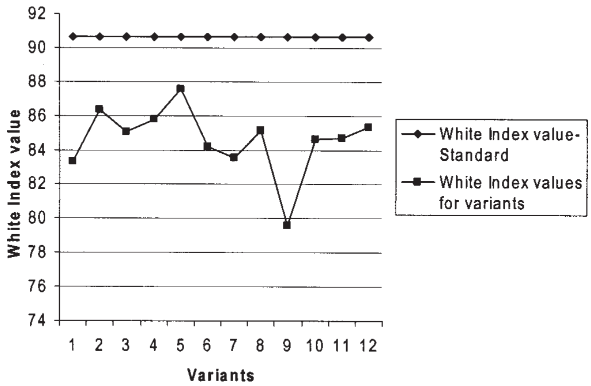

Fig. 2. White Index variation

White Index value for the reference sample Standard is 90.63. This is the target for our variants. Only V5 variant has a closer value with this Standard, 87.54.

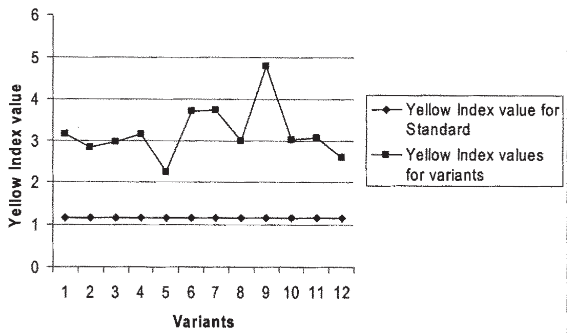

Fig. 3. Yellow Index variation

The shades, filler materials and hiding power substances are measured in quantitative terms the value of an index called yellow size. This is measured by the method described in DIN 6167 from the reflectance values Rx, Ry, Rz with this formula:

$$(Rx-Rz)/Ry \qquad (2)$$

where:

Rx - red filter reflectance;

Table 5
DIFFERENCE MEASUREMENTS CIE

CIE L*a*b* Color Difference
Date: 04-Feb-08

Standard Name: STANDARD Illuminant/Observer: D65 10 Deg
Standard Coordinates: L* = 97.41 a* = -0.06 b* = 0.63 C* = 0.64 h = 95.08

Batch Name	DL*	Da*	Db*	DC*	DH*	DE*
V1	-0.90	-0.19	1.13	1.14	0.05	1.45
V2	0.26	-0.54	1.12	1.21	0.26	1.27
V3	-0.06	-0.63	1.22	1.34	0.30	1.37
V4	0.33	-0.52	1.28	1.37	0.23	1.43
V5	0.13	-0.45	0.76	0.85	0.25	0.90
V6	0.34	-0.69	1.65	1.76	0.28	1.82
V7	0.06	-0.60	1.63	1.72	0.24	1.73
V8	-0.10	-0.48	1.18	1.25	0.22	1.28
V9	-0.71	-0.36	2.08	2.11	0.08	2.23
V10	-0.29	-0.49	1.19	1.27	0.22	1.32
V11	-0.25	-0.44	1.20	1.26	0.19	1.30
V12	-0.44	-0.44	0.94	1.01	0.22	1.13

Rz - blue filter reflectance;
Ry - green filter reflectance.

Negative values for yellow index indicate a blue tempt, positive values - a yellowish tempt. It can easily be seen from reflectance gradient of the curve if there is a yellowish tempt (= positive increase) or blue tempt (= negative increase). The Yellow Index value for Standard reference sample is 1.15. This is our target in this study. Only V5 has a closer value, 2.53. If this value is lower then the paint is less yellow, so our target is to have a better Whiteness Index and a less Yellowness Index.

Reflection values

The brightness, which is measured according to DIN 53163 at a wavelength of 520 nm, gives indication about the optical properties of the product, the scope and can give the user an estimating of purity product.

The term "brightness" that is very important for paints manufacturers, also require a clarification. According to ISO 2470, the degree of brightness is measured at a wavelength of 457 nm that correlates best with the physiological impression of human eye, while at the 520 nm, the wavelength where the brightness is measured , the eye presents high sensitivity.

The measurements differences - dL and dE- for all twelve variants compared with those of standard reference are presented in table 5.

The dE represent the error of sample tested against the standard, which is considered optimal to 0, the center axis. It can be accept an error around the center of max + / - 1 of these samples. So, V5 has an error until max. 1, which corresponds to the requirement and that can be easy changed to have a decrease value of dE. dL should have positive value, so the positive values are for V5 and V7 variants, closest to 0, but V7 falls because has a dE bigger than Standard.

Conclusions

From the twelve variants produced, analyzed and studied, only the V5 variant is still the subject of another study with the same theme, but with the aim to improve this formulation to make an interior paint according to the market requirements of paint and varnish. In this case it can be said that sodium aluminum silicate, can successfully replace titanium dioxide, using a higher percentage than we did in this formula. An improvement of the paint may consist in maintaining constant the ratio of titanium dioxide and sodium aluminum silicate and adding some other types of fillers in combination with them.

One thing is certain, namely that: sodium aluminum silicate - partial replacement of titanium dioxide, offers the following advantages when added to a paint:

- improves the optical properties (white index and high opacity);
- reduces the cost price of paint;
- improves the rheology character of paint: a higher stability during storage, *p*H stabilization, being also an anti-deposition agent;
- improves paint properties: resistance to water and to wet scrub and also a resistance to atmospheric agents.

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Manuscript received: 6.11.2009