OPTIMISING THE CORROSION PROTECTIVE ABILITIES OF MICACEOUS IRON OXIDE CONTAINING PRIMERS

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ABSTRACT

Lamellar micaceous iron oxide paints are successfully employed to provide longlife corrosion protection for metallic structures when exposed to highly aggressive environments.

The aim of this work was to formulate and manufacture lamellar micaceous iron oxide paints, to be used for the protection of steel structures exposed to water. Several formulation and manufacturing variables were taken into account.

Many paint films fail when they are saturated with moisture and blistering is a common failure because primers usually are not designed to allow the liquid to dissipate back out through the film. Consequently the film can not resist the formation of projections which result in local adhesion loss.

For maximum durability, primers must be properly formulated and manufactured. Film permeability, which depends on paint composition (pigment volume concentration) and micaceous iron oxide dispersion time, seems to be the key characteristic controlling subsequent coating performance.

Laboratory results indicated that lamellar micaceous iron oxide is a pigment which provides an anticorrosive action by providing a barrier effect. Film permeability must be compatible so as to attain a satisfactory rusting and blistering resistance.

Key words: lamellar micaceous iron oxide, pigment volume concentration, dispersion time, average particle size, blistering, rusting.

INTRODUCTION

Lamellar micaceous iron oxide paints have been used worldwide for many years to provide longlife corrosion protection for metallic structures exposed to very highly aggressive environments, such as marine and industrial service conditions. Some of the most important civil engineering structures are protected by means of lamellar micaceous iron oxide coatings.

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Lamellar micaceous iron oxide is a natural mineral; its chemical composition consists essentially on pure Fe_2O_3 which must be of an unusual crystalline form capable of fracturing into very thin platelike cleavage fragments called lamellae so as to produce the best protective action (1-4).

When a paint based on lamellar micaceous iron oxide is applied to a surface the flaky pigment particles orientate themselves in multiple layers roughly parallel to the substrate in such way that interleaving and overlapping take place. Many types of specular grey iron oxide are available but do not conform the main requirement: a flaky structure similar to mica.

In the absence of a lamellar crystal morphology, particle orientation and foliation within the paint film are not possible and the coating will not function so effectively as genuine lamellar micaceous iron oxide paints. Pigments containing large proportions of granular particle cannot form a multi-layered barrier against moisture and pollutants or preserve the binder so effectively from U.V. radiation from sunlight (5).

The objective of this project was to optimize the abilities of corrosion-inhibiting paints pigmented with lamellar micaceous iron oxide since similar compositions but with different pigment dispersion degree led to paints variable performance in service.

COATINGS FORMULATION AND MANUFACTURE

In this study, titanium tannates were used as corrosion-inhibiting pigment in polyamineamide cured epoxy coatings. In all cases, other two pigments were used together: micaceous iron oxide and micronised talc, 70/30 ratio in volume. The inhibitor/inert pigments ratio was 40/60 in volume.

Connected with the pigment level, several pigment volume concentration values (PVC) were considered: from 35 to 50 % (5 % gradations).

Paint manufacture was performed in duplicate at laboratory scale by employing a porcelain jar ball mill of 3.3 liter capacity. Mill conditions were specially considered to achieve an efficient pigment dispersion (6). First, a solution of epoxy base in the solvent mixture was prepared with stirring; the ball mill was loaded with the solution and the titanium tannates/micronised talc were added. These components were milled for 24 hours. Then, the micaceous iron oxide was added to the ball mill; several dispersion times (120, 160, 240, 360, 440 and 520 hours) were used for attaining different particle diameters of the micaceous iron oxide. Subsequently, final dispersion times for each formulation were selected, giving average particle diameters of 28, 32, 36 and 40 μm (7). After pigment dispersion, the rheological agent was added by a high speed agitation. Finally, the hardener was mixed with the base of the paint in the ratio suggested by the manufacturer (2:1 epoxy base/ hardener ratio by weight).

ESTIMATING CRITICAL PIGMENT VOLUME CONCENTRATION VALUES (CPVC)

Optical microscopy was used to evaluate the degree of dispersion of the micaceous iron oxide. The average particle diameter was calculated for each dispersion time using the expression $D = \Sigma ViNiDi / \Sigma ViNi$, where Ni is the number of particles of Di diameter present in the system and Vi the particle volume considered as spherical. Since paint flow properties are modified by the dispersion degree, viscosity was measured by a rotational viscometer provided with several measuring systems at 0.89 s^{-1} shear rate (20.0 ± 0.1 ºC temperature).

The evaluation of the water vapor permeability was carried out on free films (70-80 μm dry thickness) using the Gardner method. The quantity of water that permeated through the film under steady state conditions at 25 ºC was determined gravimetrically. Finally that quantity of water was expressed as weight per unit area and time (8).

Film permeability data corresponding to freshly manufactured paints versus different pigment volume concentration values were plotted for several particle sizes. Critical pigment volume concentrations were estimated for each average diameter.

LABORATORY TESTS

SAE 1010 steel plates of 150 x 80 x 2 mm were used. The substrate surface was sandblasted to Sa 2 ½ (Swedish Standard SIS 05 59 00/67); and the roughness profiles, measured with a Hommel Tester model T 1000, indicated a maximum roughness (Rm) of 40 μm. The steel sheets then were degreased with toluene and covered with the experimental paints by brushing. The dry film thicknesses were measured with an Elcometer Model 300 by using a bare plate and thickness standards as reference; the mean value was 70-80 μm after application of two coats with an interval of 24 hours between them. Tests were performed seven days after the application of paints to allow for curing of the coatings. The temperature of testing was 20 ± 2 ºC.

Degree of rusting. The prepared panels were placed in a salt spray chamber adjusted to ASTM B 117 Standard: temperature 35 ºC and continuous spraying with 5 % NaCl solution of pH 6.5-7.2. All panels were assessed after 1000 and 2000 hours of exposure determining degree of rusting according to ASTM D 610 Standard. The scale ranges from 0 (approximately 100 % of the surface rusted) to 10 (no rusting or less than 0.01 % of the surface rusted); intermediate values were also considered. Tests were carried out in duplicate and then mean values were estimated.

Practical film adhesion. The evaluation was made by employing an Elcometer Tester Model 106, according to ASTM D 4541 Standard. A dolly was bonded to the coating film under test and is subjected to a progressively increasing stress at constant rate until the fracture is reached. Practical film adhesion and wet film adhesion were assessed on oldes films i.e. coatings samples that have exposed in the salt spray chamber after 1000 and 2000 hours. Ten determinations were normally made at room temperature (20 ± 2ºC) on each panel to minimize the result scattering. The fracture values were expressed in $kg.cm^{-2}$.

Degree of blistering. Coated panels were also placed in an enclosed chamber containing a heated, saturated mixture of air and water vapour according to ASTM D 2247 Standard. The surfaces were observed after 1000 and 2000 hour testing. The degree of blistering was evaluated by using ASTM D 714 Standard; blistering corresponded to the osmotic phenomenon promoted by water diffusion through the coat film and not from rusting (9-13). This test was also made in duplicate.

RESULTS AND DISCUSSION

Preliminary tests

The main characteristics of corrosion-inhibiting pigments incorporated in the paint composition are displayed in Table I. Both show a low oil absorption value, which allows the incorporation of high contents of pigments in the formulation.

Photomicroscopic analyse allowed the determination of the particle size distribution of lamellar micaceous iron oxide in each manufactured sample and subsequent calculation of the average particle size value. The values for the lamellar micaceous iron oxide, for each corresponding pigment volume concentration and initial dispersion time considered, are shown in Figure 1.

A higher decrease of particle size was attained with shorter micaceous iron oxide dispersion time. It also was observed that a longer dispersion time at higher pigment concentration was required in order to obtain a given average particle size. However higher dispersion times than those considered in this work would not affect the particle size appreciably.

Viscosity of mill base was also measured; experimental results indicated that viscosity fell with increased dispersion time (i.e. viscosity decreased as average particle diameter also decreased), Figure 2.

After completion of the tests, Figure 1 allowed dispersion times to be established for pre-determined particle sizes of micaceous iron oxide; these values are shown in Table II. Consistent micaceous iron oxide paints could then be manufactured, under similar ball mill operative conditions, for those dispersion times (14).

The water vapor permeability of the films for each dispersion time (average particle diameter) for each PVC value are shown in Figure 3. These values can be represented graphically with respect to pigment volume concentration for each average particle diameter in order to estimate the corresponding CPVC value. Figure 4 shows the methodology for a paint with 40 μm micaceous iron oxide diameter; and the results are included in Table II. The influence of particle diameter on CPVC value is attributed to the ability of the pigment to achieve a high packing density: i.e. as particle size increased the restrictive effect also increased and, as a consequence, the CPVC value diminishes.

Degree of rusting and practical film adhesion

Results are assembled in Table III. These experimental values were statistically treated according to factorial design of the 4 x 4 type (4 PVC values and 4 micaceous iron oxide average diameters), that is 16 combinations. Each combination was prepared and tested in duplicate (replicas). The values indicated in Table III enabled estimates to be made of the variance and then the Fisher test (15). Reference tables (16) indicate that the variables considered in this study (micaceous iron oxide average diameter and PVC value) showed a meaningful influence on the coating behaviour. To interpret the results, the total values corresponding to each effect studied were calculated for 1000 and 2000 hours of testing, Table IV.

The results indicate that in order to reach the best behaviour in the tests (the highest total value), it would be necessary to select a PVC of 40 or 45 % and a micaceous iron oxide average diameter of 28 μm. Considering the PVC effect in both tests, the 35 and 50 % best samples showed a significant inferior performance. Concerning micaceous iron oxide average diameter, 32, 36 and 40 μm displayed a pro-rate decrease in effectiveness as compared to the 28 μm coating sample.

For the tests performed on aged panels, the results showed a significant influence of the variables considered. The points evident from these data and the observations made during the tests are:

- For all paints formulated with low pigmentation levels, excellent corrosion resistance and practical adhesion were observed, indicating that the incorporation of pigment led to a better adhesion performance. For pigment volume concentration values higher than the critical one, corrosion resistance and practical adhesion decreased significantly as the pigment volume concentration was increased.

- Practical adhesion tests indicated that in general, films with low pigment volume concentration failed cohesively (break in the body of the paint film) and the extent of this failure decreased as pigment volume concentration increased. At critical pigment volume concentration, failure was completely adhesive (break between the paint film and the substrate). At pigment volume concentration higher than the critical value, the failure became cohesive again. It is possible that the thin platelets of lamellar micaceous iron oxide was the responsible for the high adhesion and cohesion performance.

- The average diameter of the micaceous iron oxide particles influenced the practical adhesion as well as the corrosion resistance. A lower particle size (higher dispersion time) led to better performance.

Degree of blistering

Results obtained on panels aged in 100 % Relative Humidity Cabinet after 500 and 1000 hours are also shown in Table III.

Experimental values indicate improved blistering resistance with increasing micaceous iron oxide particle size and pigment content. Thus, micaceous iron oxide primers with pigment volume concentration values near or higher than critical ones displayed a very good blistering resistance (no blistering, value 10) meaning no liquid or gas filled projections (no swelling from rusting was considered). Film permeability data were consistent with this behaviour.

The low solubility of both micaceous iron oxide and titanium tannates decreased the susceptibility of coatings to osmotic moisture permeation.

Simultaneous analysis

Results obtained in salt spray chamber (degree of rusting and practical film adhesion) and in 100 % relative humidity cabinet (degree of blistering) indicated that the best performance would be attained with Primer number 4 (PVC 50 % and micaceous iron oxide average diameter 28 μm), Primer number 7 (PVC 45 % and average diameter 32 μm), and Primer number 11 (PVC 45 % and average diameter 36 μm); though other primers showed good performance in the quoted comparative tests. However, confirmation lasts will be required to define the most efficient primer for each particular condition.

CONCLUSIONS

Primers often are formulated to be barriers, in order to isolate the metallic substrate from the environment. However, all organic coatings are more or less permeable to moisture and pollutants, and as such they are not perfect barriers.

Many paint films fail when they are saturated with moisture and blistering is a common failure because primers usually are not designed to allow the liquid to dissipate back out through the film. Consequently the film can not resist the formation of projections which result in local adhesion loss.

For maximum durability, primers must be properly formulated and manufactured. Film permeability, which depends on paint composition (pigment volume concentration) and micaceous iron oxide dispersion time, seems to be the key characteristic controlling subsequent coating performance.

Laboratory results indicated that lamellar micaceous iron oxide is a pigment which provides an anticorrosive action by providing a barrier effect. Film permeability must be compatible so as to attain a satisfactory rusting and blistering resistance. Micaceous iron oxide is also attractive because it is non toxic, non flammable; its use involves no particular hazard to manufacturing operatives or to paint users.

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Table I

Characteristics of corrosion-inhibiting pigments

		Micaceous iron oxide	**Titanium tannates**
Physical properties	Density, g.cm^{-1}	4.82	1.51
	Oil absorption,g/100 g	20.3	20.2
Chemical composition	Ferric oxide, %	86.5	--
	Silica, %	5.8	--
	Aluminium oxide, %	4.0	--
	Magnesium oxide, %	1.3	--
	Calcium oxide, %	0.6	--
	Titanium (IV) ion, %	--	1.3

Table II

Dispersion time for attaining pre-established particle sizes of micaceous iron oxide

Paint	**Average diameter, μm**	**PVC, %**	**Dispersion time, minute**	**Estimated CPVC, %**
1	28	35	216	50.0
2		40	310	
3		45	380	
4		50	520	
5	32	35	168	47.2
6		40	247	
7		45	306	
8		50	424	
9	36	35	120	45.0
10		40	204	
11		45	256	
12		50	352	
13	40	35	88*	43.8
14		40	168	
15		45	206	
16		50	314	

*Extrapolated value

Table III

Laboratory tests

Primer	Degree of rusting(1) (ASTM D 610)		Degree of blistering(2) (ASTM D 714)		Practical adhesion(1), kg.cm^{-2} (ASTM D 4541)	
	1000 h	2000 h	500 h	1000 h	1000 h	2000 h
1	10	10	6-M	4-MD	26	24
2	10	10	8-M	6-MD	27	26
3	10	10	9-M	8-M	29	28
4	10	9	10	10	32	29
5	10	10	9-M	8-M	25	24
6	10	10	9-M	8-M	26	25
7	10	10	10	10	28	27
8	9	7	10	10	23	21
9	10	10	9-F	8-M	26	23
10	10	10	10	9-F	28	25
11	10	10	10	10	29	26
12	8	6	10	10	20	17
13	10	10	10	9-F	25	22
14	10	10	10	9-F	26	23
15	10	9	10	10	21	19
16	6	5	10	10	12	10

(1) Salt spray chamber, ASTM B 117 Standard
(2) 100 % Relative Humidity Cabinet, ASTM D 2247 Standard

Table IV

Total values of degree of rusting and practical film adhesion for each effect

Effect	**Level**	**Degree of rusting***		**Film adhesion**,Kg.cm^{-2}**	
		1000 h	2000 h	1000 h	2000 h
Micaceous iron oxide Average diameter, μm	28	40	39	114	107
	32	39	37	102	97
	36	38	36	103	91
	40	36	34	84	74
Pigment volume concentration, %	35	40	40	102	93
	40	40	40	107	99
	45	40	39	107	100
	50	33	27	87	77

* Salt spray chamber

** Panels aged in salt spray chamber

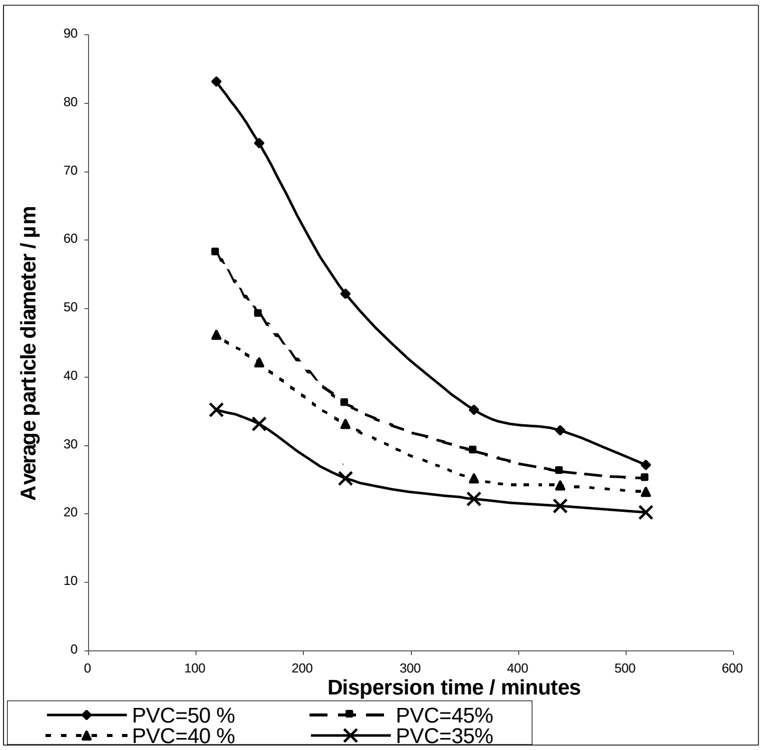
CAPTIONS

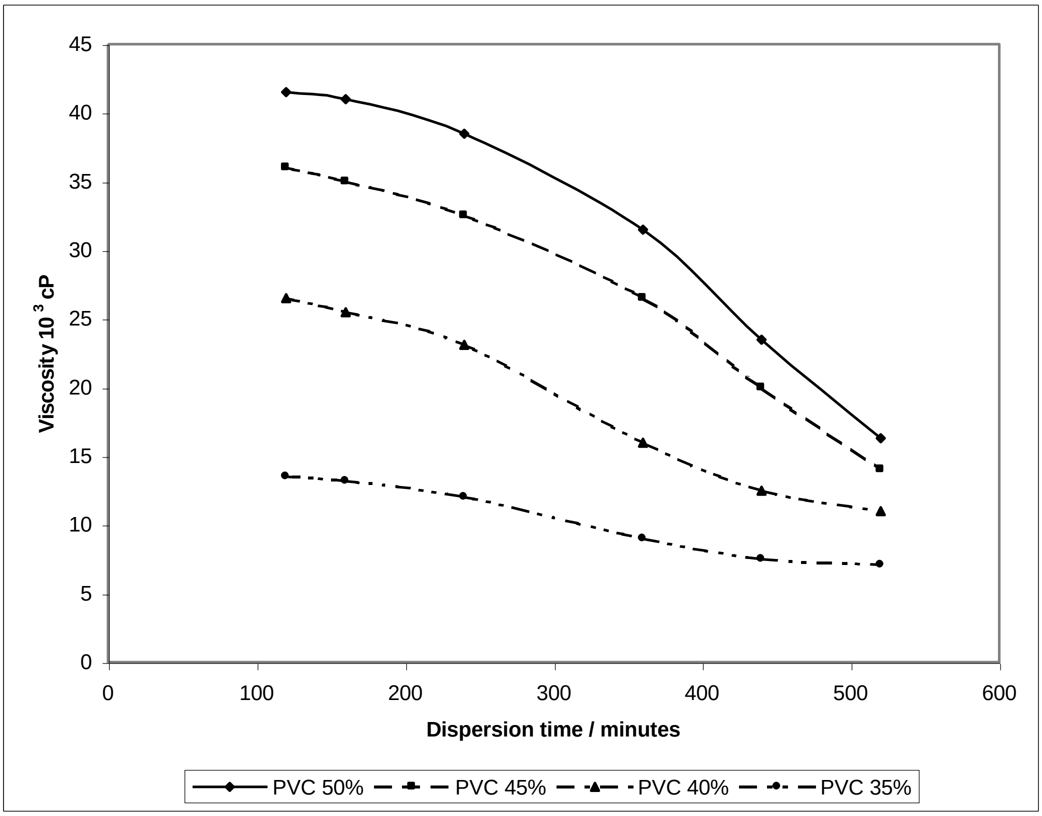
Figure 1.- Average particle diameter of micaceous iron oxide (μm) as a function of dispersion time (minutes).

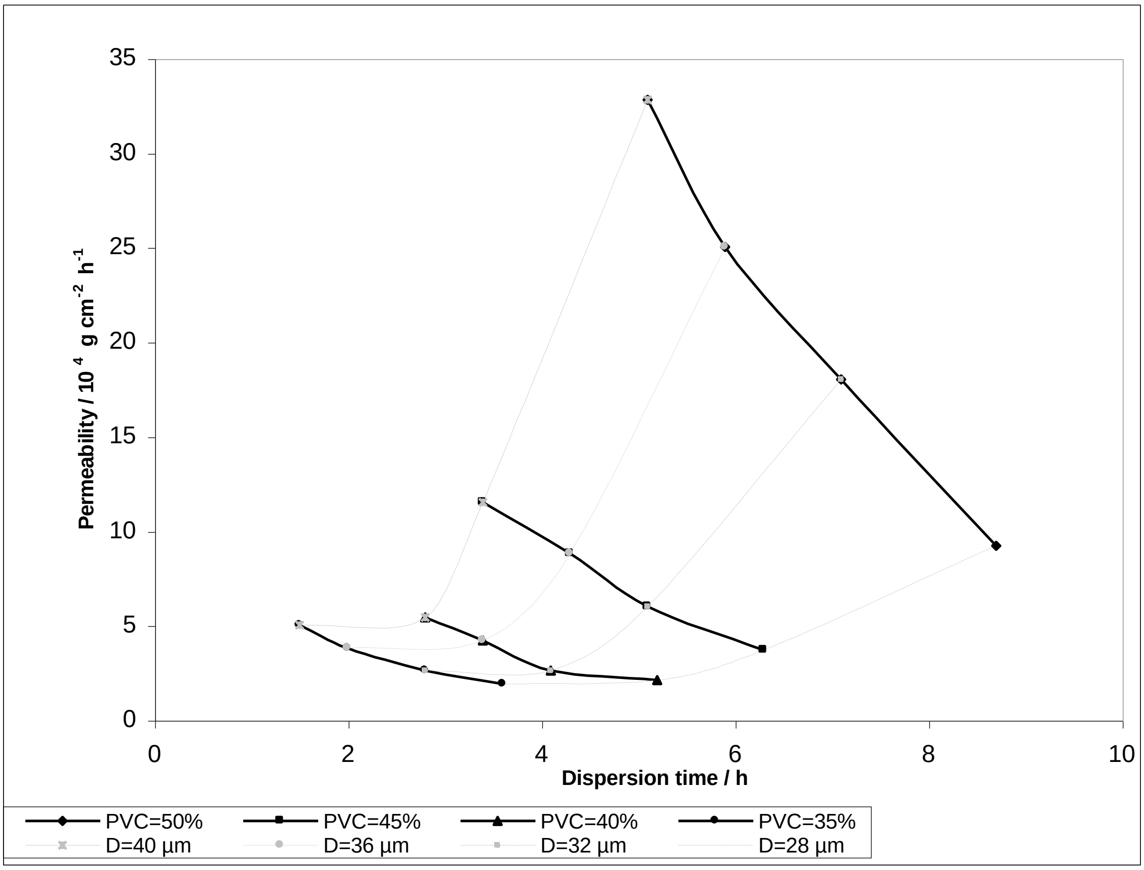
Figure 2.- Mill base viscosity at $\gamma = 0.89^{s-1}$ (10^{+3}cP) versus dispersion time (minutes).

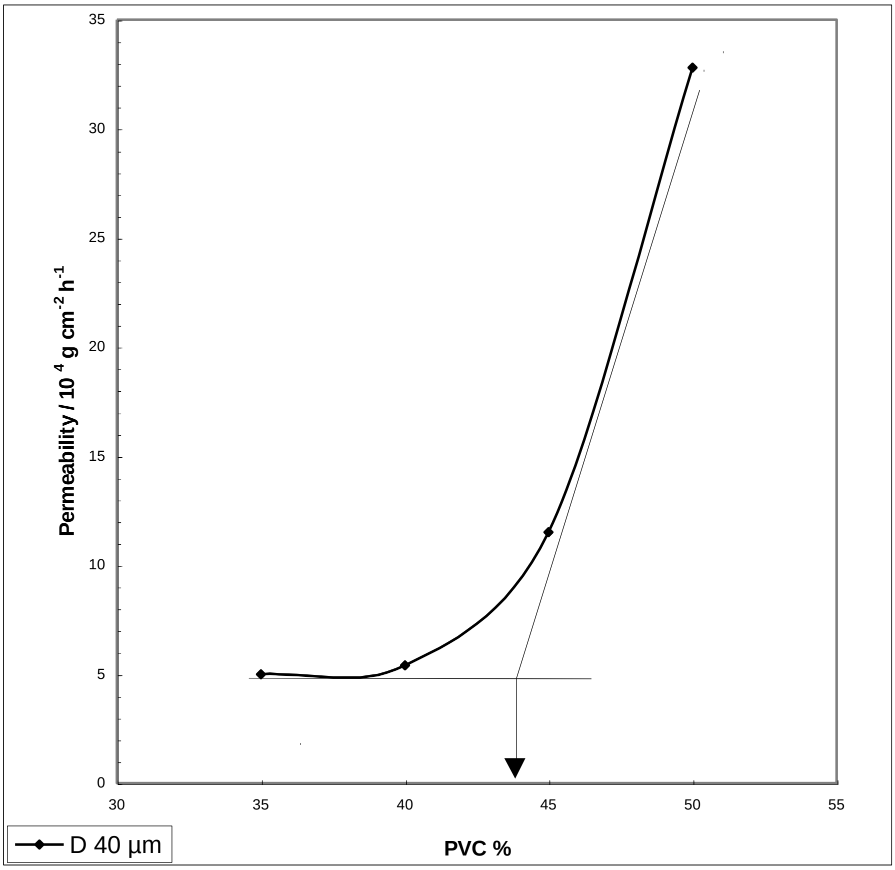
Figure 3.- Film permeability (10^4 g cm^{-2} h^{-1}) versus dispersion time (h), 70-80 μm dry film thickness.

Figure 4.- Film permeability (10^4 g cm^{-2} h^{-1}) versus pigment volume concentration % : graphic estimation of CPVC value.


90
80
70
60
50
40
30
20
10
0
Average particle diameter / µm
0
100
200
300
400
500
600
Dispersion time / minutes
PVC=50 %
PVC=45%
PVC=40 %
PVC=35%


45
40
35
30
25
20
15
10
5
0
Viscosity 10^3 cP
0
100
200
300
400
500
600
Dispersion time / minutes
PVC 50%
PVC 45%
PVC 40%
PVC 35%


35
30
25
20
15
10
5
0
Permeability / 10 ^{4} g cm^{-2} h^{-1}
0
2
4
6
8
10
Dispersion time / h
PVC=50%
PVC=45%
PVC=40%
PVC=35%
D=40 µm
D=36 µm
D=32 µm
D=28 µm


Permeability / 10 ^{4} g cm^{-2} h^{-1}
35
30
25
20
15
10
5
0
30
35
40
45
50
55
PVC %
D 40 µm