

# Federation Series on Coatings Technology

Unit Twenty-Seven  
Anti-Corrosive  
Barrier  
And Inhibitive  
Primers



FEDERATION  
SERIES ON  
COATINGS  
TECHNOLOGY

Unit Twenty-Seven

Anti-Corrosive  
Barrier  
And Inhibitive  
Primers

By  
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## ABOUT THE AUTHOR

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He has published numerous papers and has lectured extensively on coatings technology and corrosion science to professional societies, universities, and a number of private corporations. He is the author of several patents. Mr. Hare is an active member of the National Association of Corrosion Engineers, The Oil and Color Chemists' Association and the New England Society for Coatings Technology.

## ANTI-CORROSIVE BARRIER AND INHIBITIVE PRIMERS

In Unit 26 of this Series, an attempt was made to present the basic principles of the corrosion mechanism and examine some of the methods used to modify and so retard the corrosion process. It was shown that organic coatings might be effectively employed towards this end in any one of three ways.

(1) *By Resistance Inhibition (Barrier Primers)*, where thick impermeable films are used to reduce the access of corrosive electrolytes to the metal and impede corrosion by artificially increasing the electrical resistance of the corrosion cell.

(2) *By Anodic and/or Cathodic Polarization (Inhibitive Primers)*, where small quantities of soluble species from the primer film are dissolved as moisture diffuses through the coating to the metal where they artificially increase the polarization of the anode and/or the cathode.

(3) *By Cathodic Protection (Zinc Rich Primers)*, where films of highly zinc loaded coatings are employed as conductive anodes which sacrificially corrode to maintain steel cathodic and protected.

In this Unit the Barrier Primer and the Inhibitive Primer will be examined in detail. The Zinc Rich Primer will be treated separately in a future Unit.

### I. INTRODUCTION

In any coating system, each component (pretreatment, primer, finish coat, etc.) fulfills its own necessary role as part of the properly functioning system. Without any one component the total system is rendered less effective to a greater or lesser extent. If there is one component of the anti-corrosive system that is

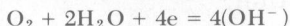
of paramount importance, however, it must be the primer. This must bear the brunt of the responsibility for corrosion control and, in many cases, for adhesion. Surface preparation and conversion coatings (when they are present) function as mere preliminaries, preparing the substrate for the primer coat, while one of the finish coats two principal responsibilities is to protect the primer from the environment, thus prolonging its effective service life.

In many low cost, albeit short lived, paint jobs, surface preparation is entirely omitted. In other systems, conversion coatings may be unnecessary and even deleterious, while in still others the primer may be placed in service without a finish coat. It may be argued that it is equally likely (especially in cheap industrial finishing) for the primer to be omitted and the finish coat applied directly to the steel. However, in such circumstances, the finish becomes as much primer as finish. The primer coat is defined as "the paint or analogous substance applied next to the surface of the material being painted."<sup>1</sup> If a metal surface is painted, it is by definition, therefore, primed. Finish coats applied directly to the steel are crude examples of the barrier primer, the simplest of the three types of primer.

## II. THE BARRIER PRIMER

The barrier primer protects the metallic substrate by resistance inhibition, i.e., by increasing the electrical resistance between the metal surface and the electrolyte (environment), thus reducing the corrosion current to a negligible level, if not entirely preventing its flow.

In that the barrier primer also reduces the access of oxygen and moisture to the steel, thus inhibiting the cathode reaction,



the primer may also be described as protecting via cathodic inhibition. Unfortunately, protection by this mechanism is seriously curtailed by the high rates of oxygen and moisture transmission through most coating films. This occurs not only through pinholes, holidays, and other obvious macropores, but also through the general coating film continuum. In highly pigmented systems, this will occur through the interstices between the pigment particles. In low pigmented systems, it takes place at the molecular level through sites such as hydratable polar groups that are more conducive than the general vehicle continuum to

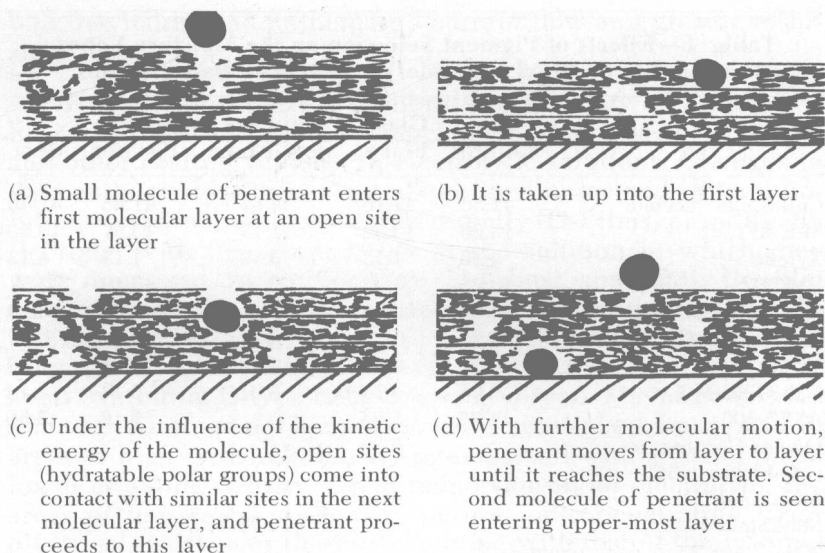


Figure 1. Migration of moisture through a coating system

the attachment of water molecules. Once affixed within the continuum, the penetrant molecule works its way through the film via similar sites at lower levels of the film strata until it reaches the metal. This movement is fostered principally by osmotic and electroendosmotic pressures in combination with the constant thermally induced movements and vibrations of the coating film molecules (Figure 1).

It has been shown that unpainted steel will be converted to rust in an industrial environment at a rate of  $0.07 \text{ g Fe/cm}^2/\text{year}$ .<sup>2</sup> The formation of  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  from  $0.07 \text{ g Fe/cm}^2/\text{year}$  would require  $0.11 \text{ g H}_2\text{O/cm}^2/\text{year}$  and  $0.03 \text{ g O}_2/\text{cm}^2/\text{year}$ . From the work of Mayne and others,<sup>3,4</sup> it is quite clear that such figures are well below the moisture and oxygen transmission rates of normal coating films. Even the low permeability asphaltics have moisture vapor transmission rates of  $0.13 \text{ g H}_2\text{O}/100 \text{ m/cm}^2/\text{year}$  (at  $25^\circ\text{C}$ ) and oxygen transmission rates of  $0.04 \text{ g O}_2/100 \text{ m/cm}^2/\text{year}$  (at  $25^\circ\text{C}$ ). It is simply not possible to prevent access of water and oxygen to the metal (thus suppressing the cathode reaction) by the use of the barrier primers. By careful formulation, however, by judicious selection of vehicle, pigment (see Table 1) and, most importantly, by the application of thick films, rates of transmission of the barrier can be reduced. These techniques will be treated in more detail shortly.



**Table 1—Effects of Pigment Selection on the Moisture Vapor Permeability Of Vinyl Chloride/Vinyl Acetate Barrier Films<sup>a</sup>**

	Control	Glass Flake	Stainless Steel Flake	Aluminum Powder	Mica
Cellosolve <sup>®</sup> acetate	41.56	41.18	38.87	41.28	41.30
M.E.K.	13.66	13.52	12.77	13.57	13.58
Xylene	4.16	4.12	3.89	4.13	4.13
VMCH <sup>b</sup>	13.25	13.47	13.90	13.49	13.51
Diisodecyl phthalate	3.30	3.35	3.46	3.36	3.36
Nuospense <sup>®</sup> 657	0.24	0.24	0.25	0.24	0.24
TiO <sub>2</sub>	9.23	9.39	9.69	9.41	9.40
Cab-O-Sil M-5	3.08	3.11	3.01	3.14	3.13
ASP <sup>®</sup> -600	11.52	5.64		6.12	5.50
Owens Corning C Flakes 1/64"		5.82			
Silane A-187 <sup>b</sup>		0.16			
Stay/Steel 304 <sup>c</sup>			14.16		
Alcoa <sup>®</sup> 408 Aluminum powder				5.26	
Wet ground mica (325) <sup>d</sup>					5.85
	100.00	100.00	100.00	100.00	100.00
Water vapor transmission gms/m <sup>2</sup> /24 hr at 60°C	34.8	13.6	8.6	12.1	22.1

(a) Merriam, C.N., Ginsberg, and Kaufman, L.G., *OCCAA Proc. & News*, p 3, Jan.-Feb. (1978).

(b) Supplied by Union Carbide Corp.

(c) Supplied by U.S. Bronze, Inc.

(d) Supplied by English Mica Co.

If the barrier primer does not effectively suppress the cathode reaction, it does markedly reduce corrosion by resistance inhibition. In this case, the high ionic resistance of the coating film prevents the electrical conductance necessary to the corrosion process. It has been shown<sup>5</sup> that the diffusion of ions through the film to the metal is much slower than the diffusion of water and oxygen. Consequently, the resultant electrolyte at the metallic interface is very high in resistance and the corrosion is held to a very low rate. If, on the other hand, there are ionogenic (ion producing) materials (partially soluble pigments, additives, soaps, etc.) within the film itself, then the ingress of pure water will decrease the ionic resistance of the coating markedly as it dissolves the soluble materials. In all cases (except where such ionogenic materials are inhibitive to the corrosion process), this

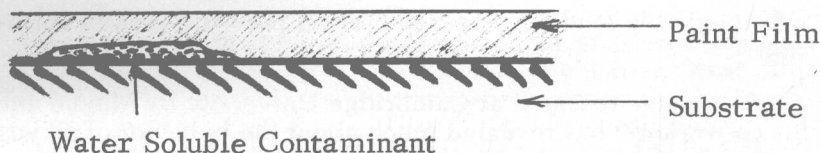
will inevitably lead to increased current flow and greater corrosion.

Extensive research at Cambridge University by Mayne and his co-workers<sup>6</sup> has revealed much about the behavior of alkyds and other coating vehicles in electrolytic solutions. Changes in the conductivity of free clear alkyd films immersed in ionic solutions were found to vary either directly (D-Films) or indirectly (I-Films) with the conductivity of the solution in which they were immersed. In the first case (D-Films), apparently the film takes up both water and the ionic species from the solution. In I-Films only water is taken up. It was further found that the type of conductivity varied considerably across the same film, some areas exhibiting D-type behavior, some I-type. Mayne concludes that such films are not homogeneously crosslinked, but consist of areas of high crosslink density interspersed with areas of much lower crosslink density. Upon immersion in an electrolyte, the areas of low crosslink density permit ionic penetration (their electrical resistances thereby changing with that of the external solution.) Conversely, areas of high crosslink density take up only water and their resistances change with the activity of water only. In a later paper,<sup>7</sup> Mayne has shown that when adherent films on iron were immersed in corrosive solutions, corrosion occurred at the D-type areas of the film having low electrical resistance.

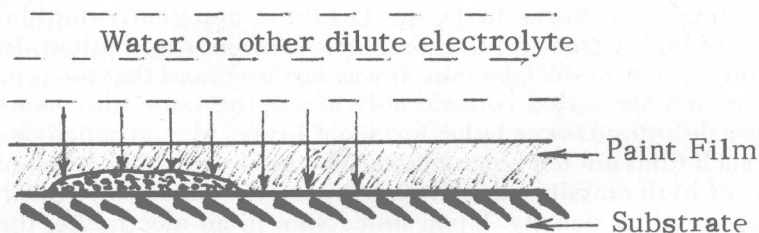
Most paint films that have been examined have been found to acquire a negative charge on immersion. This is thought to be due to the dissociation of functional ionogenic groups, mainly carboxyl, on the polymer. The negative charge then selectively attracts cations into the film.

Maitland<sup>8</sup> and Cherry,<sup>9</sup> investigating these phenomena, have shown that monovalent cations from the ionic solution penetrate the polymer and apparently undergo an ion exchange process with hydrogen ions derived from carboxyl groups on the polymer. This ion exchange process has been confirmed by radioactive labeling techniques<sup>10</sup> and chemical analysis.<sup>11</sup> Mayne has also noted that I-Films may acquire D-type behavior after being subjected to the ion exchange process by immersion of the film in an electrolytic solution.

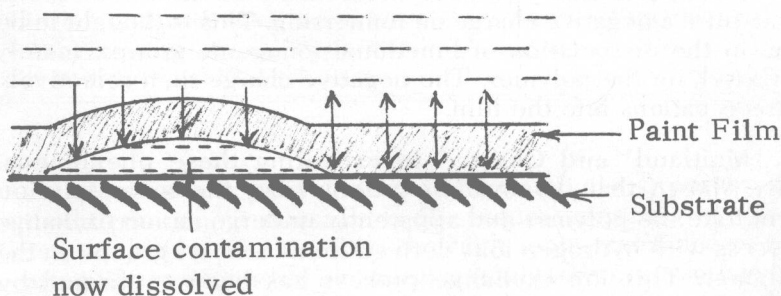
Murray,<sup>12,13</sup> investigating the ion transport in adherent epoxy/polyamide films, has indicated that the conclusions of Mayne, et al. working with free films may not necessarily apply to adherent films and that  $\text{Cl}^-$  transmission may be significant. Murray also found that a stoichiometric ratio of epoxy:polyamide



(a) Paint film is applied over a surface soiled with a water-soluble contaminant



(b) Paint film is immersed in water or a dilute electrolyte and an osmotic gradient is set up. Water passes through the paint film (a semi-permeable membrane) and begins to dissolve the surface contaminant. As the solution concentration at the metallic interface is so much greater than that outside the film, water is pulled through the film by osmosis in an effort to dilute the interface solution and so equilibrate concentrations



(c) As the solution concentration at the interface is reduced, its volume is increased to the point at which the paint film cannot contain it and the film is forced from the substrate to blister

NOTE: Where there is no surface contamination, film has absorbed water but has reached equilibrium with the environment without the occurrence of blistering

Figure 2. Mechanism of osmotic blistering

(2:1) gave much lower permeabilities than 1:1 ratio. Not only would the stoichiometric ratios result in a much higher crosslink density, the excess polyamide of the 1:1 mixes would result in a positively charged film attracting  $\text{Cl}^-$  ions. The stoichiometric epoxy/polyamide on the other hand acquires a negative charge and cation entry would be favored.

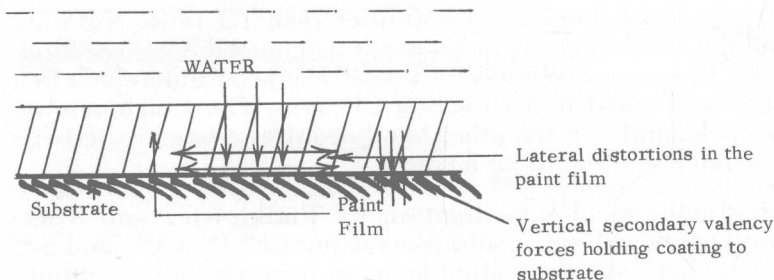
Radiochemical investigation by Fialkiewicz and Szandorowski into adherent paint films using  $\text{Cl}^{36}$  ( $\text{NaCl}^{36}$ ) and  $\text{Sr}^{90}$  ( $\text{Sr}^{90} \text{Cl}_2$ ) have shown negligible anion penetration but definite penetration of the cation,<sup>14</sup> and this is in good agreement with Mayne, Maitland, and Cherry. In the same paper, Fialkiewicz and Szandorowski show that such activated diffusion is the principal cause of cationic migration at low PVC's, but that as the PVC increases and charge density grows less (decreasing vehicle concentration), purely physical factors, such as interstitial penetration between pigment particles, become dominant.

If in properly formulated coatings, anions do not easily penetrate a coating, therefore, such species may be readily derived from the substrate. When improperly cleaned steel is coated, soluble salts, such as sodium chloride, ferrous sulphate, etc. are often entrapped at the metal/primer interface. In the presence of diffusing moisture, these salts form very efficient electrolytes which short circuit the high electrical resistance of the paint film and initiate corrosion. As the volume of the corrosion product is greater than that of the parent metal, the coating is forced from the substrate. Salts like ferrous sulphate, derived from acidic environmental contamination, may themselves oxidize and hydrolyze to form rust directly with a similar volume increase and the same effect on the paint film.<sup>15</sup> With or without the presence of water, the coating being forced from the substrate eventually breaks, exposing the steel and allowing greater access of moisture. The attack becomes progressive from this point as electroosmotic effects take over.

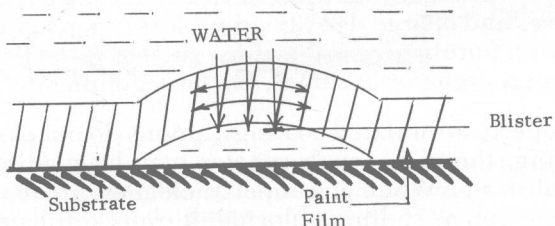
Hence, again, the importance of good surface preparation.

### Blistering

The mechanism of blistering and moisture diffusion through coating films is itself open to much conjecture despite a formidable body of research performed by some of the best authorities in coatings science. On many substrates (including metal), the phenomenon is ascribed simply to osmosis and/or the dilation of the paint film at the interface with the substrate under the influ-



- (a) Water is absorbed by a paint film, which tends to swell (some films may very slightly solvate). This causes a lateral distortion of the film with respect to the metallic substrate, which remains dimensionally stable



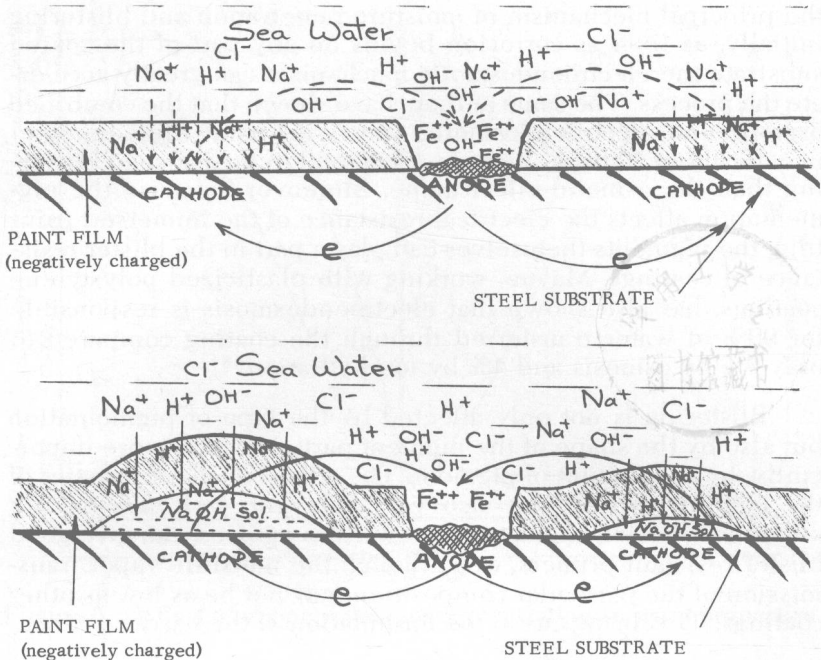
- (b) Stresses at the paint film/substrate interface arising from the distortion exceed the secondary valency forces that hold the paint to the substrate. Adhesion is lost and the paint film blisters

Figure 3. Simplified diagram of mechanism of the "paint remover effect"

ence of moisture. The water passes through the film and dissolves material from either coating or substrate. This concentration of material in solution at the substrate/coating interface raises the osmotic pressure above that of the liquid at the external interface of the coating. This sets up a solute concentration gradient with water building up under the film (in an effort to equilibrate the pressure differential) until the film eventually blisters (Figure 2). Blistering by the "paint remover effect," not necessarily contingent upon the dissolution of soluble matter, is also a possibility. In this case, the small molecules penetrate the film and accumulate at its interface with the substrate where they dilate the film, reducing its adhesion and forcing it from the substrate in a blister (Figure 3).

On metal, blistering phenomena are of far greater complexity because of attendant electrochemical phenomena. Kittelberger and Elm<sup>16,17</sup> have shown that water diffuses through the





- Paint film in sea water has absorbed water but little ionic material
- Corrosion begins to occur at a scratch, holiday, thin spot, etc. Corrosion site is anodic to surrounding steel which becomes cathodic
- For such a cell to occur, there must be a continuous ionic path through the coating film, i.e., between anode-general steel continuum-cathode-electrolyte-anode
- To achieve such a path, cations are attracted into the film (most coating films are negatively charged) dragging more water with them
- At the cathode, an excess of electrons causes a reduction in the hydrogen ion concentration (an increase in the hydroxyl ion concentration). This highly alkaline pH can cause a deterioration in adhesion and, in some films, cohesion (via saponification), resulting in blistering

**Figure 4. Electroosmotic blistering of paint films on steel**

film not only by osmotic pressure but also by an electroosmotic gradient (*Figure 4*). When a portion of the painted structure begins to corrode or is exposed to corrosion, moisture is pulled through the coating by an electrical potential gradient between the corroding area and the protected areas (of higher electrical potential) that are in electrical contact. Although osmosis may be

the principal mechanism of moisture penetration and blistering initially, as soon as corrosion begins on any part of the coated substrate the electroendosmotic mechanism can greatly accelerate the process. The same authors have shown that the combined osmotic and electroendosmotic effects on paint films on steel may be about 20 times more instrumental in the cause of blistering than the osmotic effect alone. Moreover, because the pigmentation affects the electrical resistance of the immersed paint film, the pigments themselves can play a part in the blister resistance of coatings. Mayne, working with plasticized polystyrene coatings, has also shown that electroendosmosis is responsible for 90% of water transferred through the coating compared to only 6% by osmosis and 4% by ion hydration.<sup>18</sup>

Blistering is not only affected by the type of pigmentation but also by the shape of the pigment particles, and, more importantly, by the amount of pigment. The adhesive characteristics of the coating vehicle are also very relevant. Vehicles having superior adhesion characteristics, such as epoxies, can give good blister resistant primers, even though the moisture vapor transmission of the particular composition may not be as low as other coatings. This brings us to the formulation of the barrier primer.

### Pigment Volume Concentration

One of the most basic concepts in paint chemistry is that of pigment volume concentration (PVC). This is simply the volume of pigment expressed as a percentage of the total volume of the dry coating. PVC provides a far truer picture of the condition of the dry film than does the pigment binder ratio (an expression of composition based on a weight ratio only). Unlike PVC, the pigment binder ratio bears no real relationship to the physical characteristics of the paint film. This is principally because of the wide variations in the specific gravity of pigments (1.2–9.0) and of coating vehicles (0.9–1.6).

A glance at the now classical graph (*Figure 5*) compiled by van Loo<sup>19</sup> clearly shows how the properties of a coating are affected by increasing the pigment volume concentration. At low PVC values, the pigment is considered completely wet by the vehicle and totally encapsulated in a plastic continuum. Thus, the film is glassy, impermeable (relatively), and protective, and its flexibility and tensile strength are high. As the pigment volume is increased, little happens until the volume of excess vehicle begins to decrease. Then the above properties are slowly compromised. First, the gloss is reduced as unevenly shaped

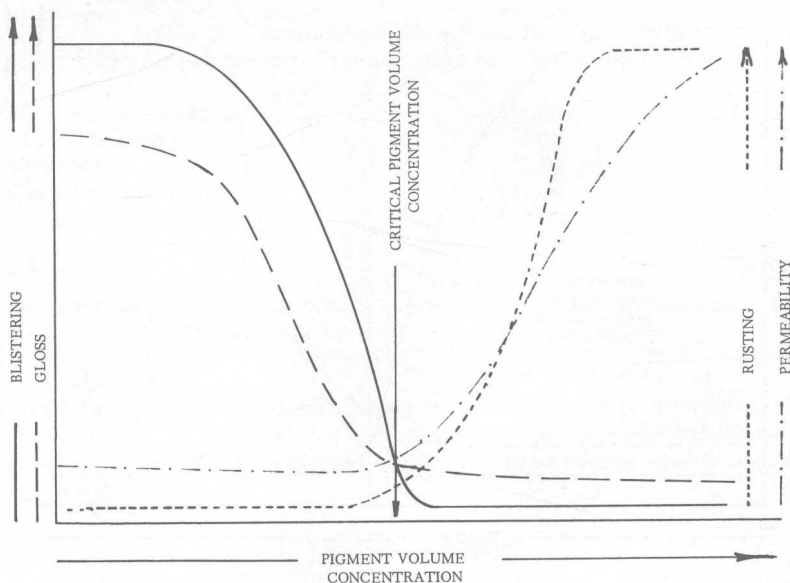


Figure 5. Effect of pigment volume concentration on paint properties

pigment particles protrude above the vehicle layer. As excess vehicle is further reduced, a point is reached at which just enough vehicle remains to coat each pigment particle and to fill all the interstices between them. This is the level of tightest possible pigment packing and is referred to as the critical pigment volume concentration (CPVC). Up to this point the gloss has been dropping, the blistering has been decreasing, and the blister size has been getting smaller. The mechanical properties have also been falling off. At still higher pigment loadings, the interstices between the pigment particles remain unfilled with vehicle, and the impermeability and protective properties of the coating film decrease dramatically. The viscosity also increases and the opacity improves markedly due to light scattering at voids. At even higher PVC, vehicle encapsulation of the pigment is reduced and the film becomes so poorly bound as to be powdery and without strength.

The formulation of both barrier and inhibitive primers, therefore, will be at PVC levels below the critical PVC (Figure 6). Differences in PVC below this level have less effect upon corrosion and permeability than might be expected, and there is evidence to support a negligible increase in moisture vapor transmission (MVT) at very low PVC's. Some workers, such as

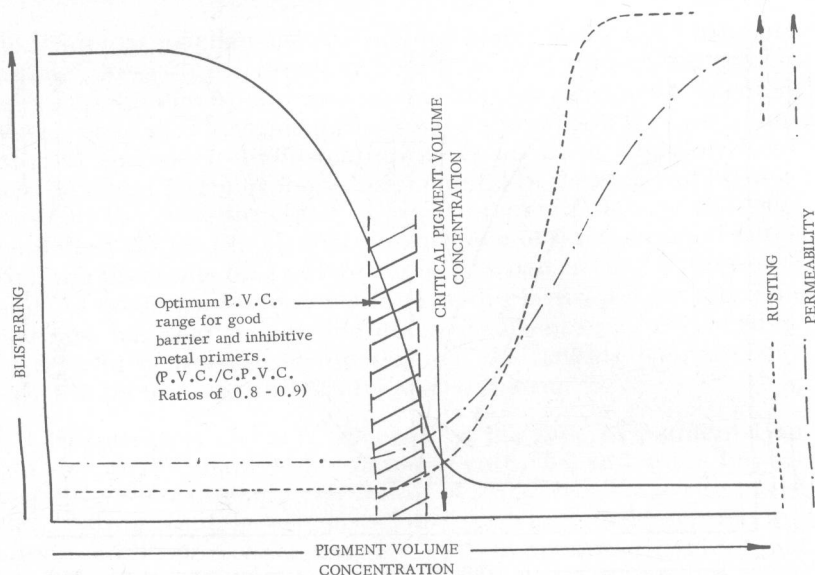


Figure 6. Pigment volume concentration of barrier and inhibitive primers

Hoogerbeets, in fact, believe that the permeability of a coating actually decreases until near the critical pigment volume concentration and only then rapidly increases.<sup>20</sup>

### Pigmentation

Although we have seen that the electrical resistance of paint films (and thus their resistance to electroendosmotic effects) may be affected by the choice of pigments, little scientific investigation of the effects of the various pigments has been made. Certainly, some pigment combinations do give increased blister resistance; strontium chromate/zinc oxide combinations, for example, give better blister resistance in both salt and fresh water immersion than many other inhibitive pigment combinations.<sup>21</sup> Whether this can be related to low electrical resistance has not been determined. Most commercial applications of the barrier technique involve straightforward physical methods to reduce blistering, i.e., they use pigments with flat, platy particles. Such pigments align themselves with the plane of the substrate while the film is wet and, when the film is dry, reduce moisture and oxygen transmission in much the same way as venetian blinds reduce the transmission of sunlight. Mica, micaceous iron oxide, glass flakes, leafing aluminum power (Table 2), and stainless