Changes in Composition and Characteristics of Latex Paints Applied On Porous Inorganic Substrates

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Changes in film composition and characteristics that occur during and/or immediately after the application of latex paints on porous inorganic substrates were investigated. Gas chromatography (GC) and thermal analysis were among the techniques used for this purpose. The changes in coalescing agent and binder content were determined by GC and thermogravimetric analysis, respectively, and the changes in glass transition temperature by differential scanning calorimetry. It was found that the type of porous substrate could significantly affect the paint composition (pigment volume concentration, coalescent level) during the film formation process.

INTRODUCTION

A variety of porous inorganic substrates, e.g., concrete, brick, and fiber/cement, are coated for protection or embellishment. Latex paints have been used for this purpose for a long time by professional painters and the "do-it-yourself" sector due to their many advantages such as low volatile organic compound (VOC), easy washing of applying equipment, and low fire hazard.

More recently the building industry has also become interested in applying latex paints, especially for coating new types of fiber/cement substrates. To maximize productivity and minimize manufacturing cost, the building industry is moving toward more automated, higher throughput manufacturing lines; but to produce paints capable of being applied under such conditions is not a trivial matter. Such paints must possess not only good durability, but also have other characteristics, such as sufficient early block, and mar and scratch resistance. Despite the continuous efforts by the paint industry to meet these requirements, appearance of premature defects such as cracking/fissuring, detachments, stains, and efflorescence are still observed.

While formulating paints for nonporous substrates, e.g., steel, is already complex, for porous substrates the task is even more difficult because the porosity and the heterogeneity of substrates must also be considered.

The general laws governing the transport of liquids and gases in porous materials are relatively well known (e.g., reference 1) and methods to measure porosity are already available (e.g., reference 2). However, due to the heterogeneity of most porous materials the general principles can rarely be applied.

Many aspects of paint penetration in wood, such as paint depth penetration, adhesion, and different aspects of durability, have been investigated.[3-6] Most studies on porous inorganic substrates were dedicated to concrete and its impregnation with polymeric materials such as polymethylmethacrylate and polystyrene.[7] It was found that depending on pore type and size, as well as on polymeric material characteristics, the impregnation fills the pores partially or totally. In general, impregnated concrete possesses lower water absorption and improved mechanical characteristics, such as flexural capacity, impact resistance, and abrasion.

To our knowledge, there has been little, or no, investigation of the effect of porous inoganic substrates on the composition of paints, and thus, on their behavior.

If paint penetration of the substrate to increase the paint adhesion is desired,[8] a possible selective penetration of paint components can change the film composition, especially during the paint application and film formation, possibly affecting the film's final properties.

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Table 1—Characteristics of Coatings and Binders

Paint	A	B	C	D
PVC (%)	18	18	18	45
MFFT, °C	22	12	12	−10
Coalescent	Without	L	L	T
Binder				
T_g, °C (calc.)	20	33	20	—
MFFT, °C	22	39	22	—

L = Lusolvan FBH; T = Texanol

In this study we were especially interested in looking at the coalescing agent, the binder, and certain additives, because they could directly affect the minimum film formation temperature (MFFT), the pigment volume concentration (PVC), and the coating stability, respectively—all parameters determining the coating durability.

EXPERIMENTAL

Materials

Organic Coatings: (A) an acrylic latex paint without coalescing agent, filled with TiO_2, carbon black, red and yellow iron oxide, and talc; (B) an acrylic latex paint containing a coalescing agent (Lusolvan FBH), and filled with TiO_2, carbon black, red and yellow iron oxide, and calcium carbonate; (C) (A) + 3% Lusolvan FBH; and (D) an acrylic latex paint containing a coalescing agent (Texanol), and filled mainly with TiO_2 and calcium carbonate. The particle size of latex binders used in this study is 80 to 100 nm.

Porous Substrates: (Ac)—a "strongly" compressed fiber/cement substrate; (ET)—a fiber/cement substrate containing organic fibers; (FB)—a fiber/cement substrate of unknown composition; (KN)—cardboard/plaster (gypsum) plates; and (BR)—brick.

Nonporous Substrate: (GL)—glass plates.

Application: by draw down at 21°C and 50% relative humidity (RH).

Instrumental Methods

Differential Scanning Calorimetry (DSC): This thermal analysis technique was used to determine the glass transition temperature (mid T_g) of paints.

A Mettler Toledo TA-8000, DSC 30 with TC-15 Station and Star System was used under the following conditions: heating rate of 20°C/min, amount of specimen ≈ 20 mg, and purge gas of dry He (50 ml/min). These measurements were made to evaluate changes in coalescing agent resulting from its penetration of the substrate.

Thermogravimetric Analysis (TGA): These measurements were made with a Mettler Toledo TA-8000, TG 50 with TC-15 Station and Star System under the following conditions: heating rate of 20°C/min, amount of specimen ≈ 20 mg, and purge gas of dry air (200 ml/min). These measurements were carried out to evaluate the binder penetration of porous substrates.

Coating Characteristics

A number of calculated or determined coating and binder characteristics are given in *Table* 1.

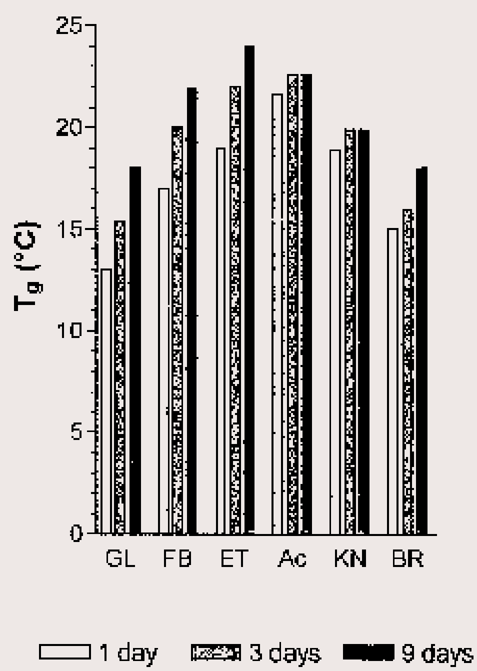

Figure 1—Paint B. T_g of the coating applied on different substrates, porous (FB, ET, Ac, KN, BR) and nonporous (GL), after different periods of drying.

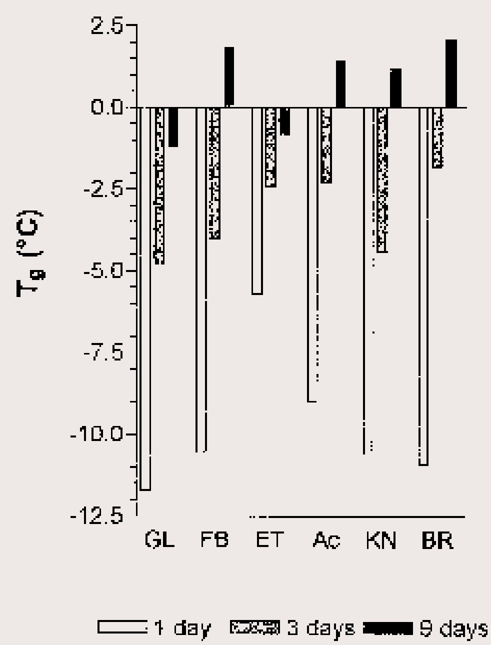

Figure 2—Paint D. T_g of the coating applied on different substrates, porous (FB, ET, Ac, KN, BR) and nonporous (GL), after different periods of drying.

RESULTS

Most latex paints contain one or more coalescing agents. They are added to the paint to decrease the MFFT to a temperature at which the coalescing process can take place.[9-13]

The coalescing process might be jeopardized by an increase in MFFT during paint application. This can result from a decrease in coalescing agent which occurs when it is absorbed by a porous substrate.

Another possible effect of a porous substrate on a coating's composition is the decrease of the binder level due to its penetration into the substrate during the paint application. Such a decrease would increase the PVC of the film, a fact that can significantly change a great number of coating characteristics, such as stress development,[14, 15] mechanical properties,[16-18] and permeability.[19]

Coalescing Agent

Since the MFFT is directly related to the T_g, we used this latter coating property to verify a possible coalescing agent penetration of the porous substrate.

The T_g was measured by DSC since a preliminary study involving a variety of techniques (DSC, thermomechnical analysis (TMA)) showed this method to be the most convenient for the coatings investigated. Briefly, the method consisted of applying paint on a substrate, removing the paint samples from the substrate with a scraper after well determined periods of time (one, three, and nine days), and then placing them in an aluminum pan before performing the DSC test.

In this part of the study we used six substrates and four paints. One substrate was not porous (GL), and one paint did not contain any coalescing agent (A).

The results obtained are presented in *Figures* 1-4. *Figures* 1 and 2 show that (a) T_g increases with time as a consequence of the evaporation of the coalescent agent from the coated substrate, and (b) during the first days of drying, T_g of paints applied on porous substrates is not only higher than that of paints applied on the nonporous substrate, but it is also dependent on the type of porous substrate. These two facts indicate that part of the coalescent agent present in the paint is absorbed by the porous substrate during paint application. After all of the coalescent agent had left the coating, it is expected that the T_g would be dependent only on the type of paint. This is so because the T_g is mainly dependent on the type of binder.

To confirm these results additional tests were carried out with two paints of identical composition except for the presence of a coalescing agent. *Figure* 3 indicates that, as expected, the T_g of the paint that does not contain coalescing agent (paint A) is practically the same regardless of the drying period (one or three days) and of the type of substrate on which it is applied (nonporous or of different porosity). On the contrary, the T_g of the paint that contains a coalescent agent (paint C, *Figure* 4) is dependent on the drying period and the type of substrate. These results indicate again the validity of the method used in this study and the reconfirmation that a porous substrate might induce changes in coalescent agent composition.

The actual amount of coalescent agent absorbed by a porous substrate was determined by gas chromatography. The procedure used was to apply paint on glass and

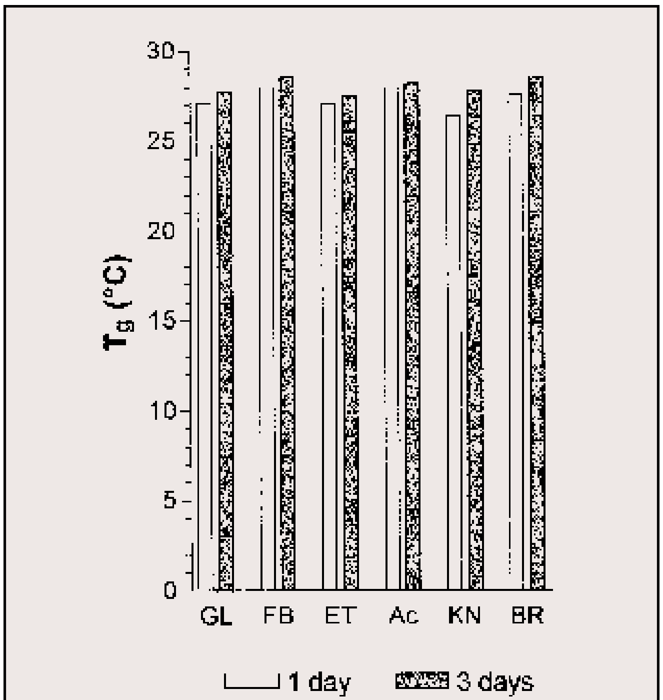

Figure 3—Paint A. T_g of the coating applied on different substrates, porous (FB, ET, Ac, KN, BR) and nonporous (GL), after different periods of drying.

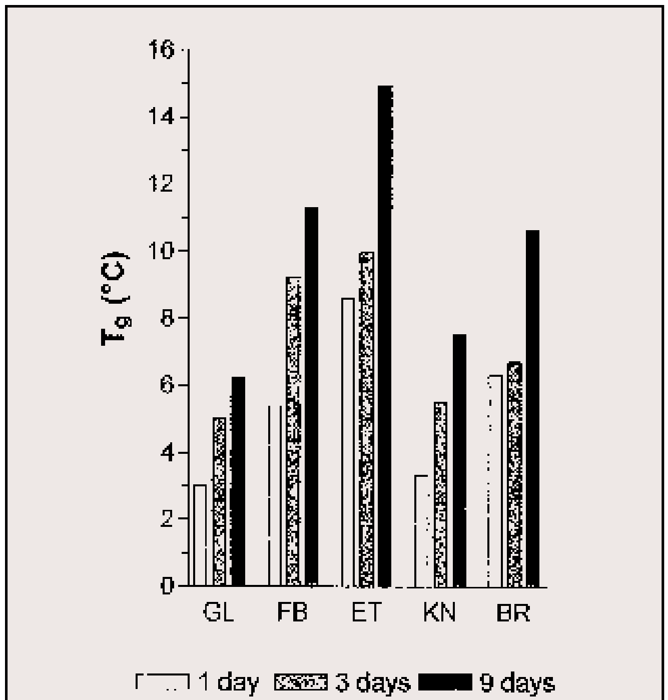

Figure 4—Paint C. T_g of the coating applied on different substrates, porous (FB, ET, KN, BR) and nonporous (GL), after different periods of drying.

Table 2—Concentration of Coalescing Agent (% per Dry Weight of Paint) in Wet Paint and After One Day of Drying: in Film, Evaporated, and Absorbed by the Porous Substrate

	Paint B[a]		Paint D[b]	
	GL	ET	GL	ET
In wet paint	6.50 (100%)[c]	6.50 (100%)	5.06 (100%)	5.06 (100%)
In film	4.81 (74%)	4.40 (67.7%)	2.70 (53.4%)	1.92 (37.9%)
Evaporated	1.69 (26%)	1.69 (26.0%)	2.36 (46.6%)	2.36 (46.6%)
In porous substrate	—	0.41 (6.3%)	—	0.78 (15.4%)

(a) Lusolvan FBH
(b) Texanol
(c) The values in parentheses represent the amount of coalescing agent with respect to the level in wet paint (100%); GL = glass; ET = fiber/cement.

a porous substrate. After one day of drying, samples of about 0.70 g were scraped away and placed in a glass container containing methanol and an internal standard (phenoxy ethanol). The gas chromatography (GC) analyses were performed seven days later. Some results are shown in *Table* 2.

Binder

The possibility of binder penetration in porous substrates was also examined. This was done with the help of the TGA technique. The procedure used was as follows. After paint was applied to various substrates and dried, paint samples were taken from the various substrates and placed in aluminum oxide crucibles. They were then submitted to a temperature sweep of up to 1000°C in the TGA. The integration of the differential TGA (DTGA) peak corresponding to the binder's thermooxidative decomposition during the heating of the sample in the TGA, and the consideration of the initial and residual weights of the sample, should allow the amount of binder in the paint to

Table 3—Binder Content (%) in the Dry Film of Two Paints Applied on Three Substrates

	Paint A	Paint E
Glass	78	47.7 (PVC 30.0%)
Substrate Ac	74	44.6 (PVC 32.6%)
Substrate ET	71	44.0 (PVC 33.1%)

be determined. Examples of such peaks are shown in *Figure* 5.

The results obtained with two paints applied on three substrates, two porous and one nonporous, give clear indications that part of the binder present in the paint is absorbed by the substrate (see *Table* 3). For example, while the binder in paint A applied on glass represents 78% of the dry film, when applied on porous substrates Ac and ET, it represents only 74% and 71%, respectively. For another paint (E) containing only binder and $CaCO_3$, the analysis of the data obtained shows that the binder content in the dry film of this paint applied on GL, Ac, and ET represents 47.7%, 44.6%, and 44%, respectively. These binder contents correspond to 30, 32.6, and 33.1% PVC for the paint applied on glass, Ac, and ET, respectively.

It is important to add that TGA tests were also performed with paints applied at different wet film thickness. They indicate that the lower the wet film thickness the higher the "apparent" binder penetration. This means that the samples investigated, i.e., scraped from the substrate, represent the dry film in its entirety, and that there is a binder profile with its lowest level at the substrate interface. We expect, therefore, that the real PVC of the paint near the interface with the porous substrate would be higher than those mentioned previously.

Effect of Other Paint Components

To verify the conclusions concerning the coalescent penetration in porous substrates and possibly find inter-

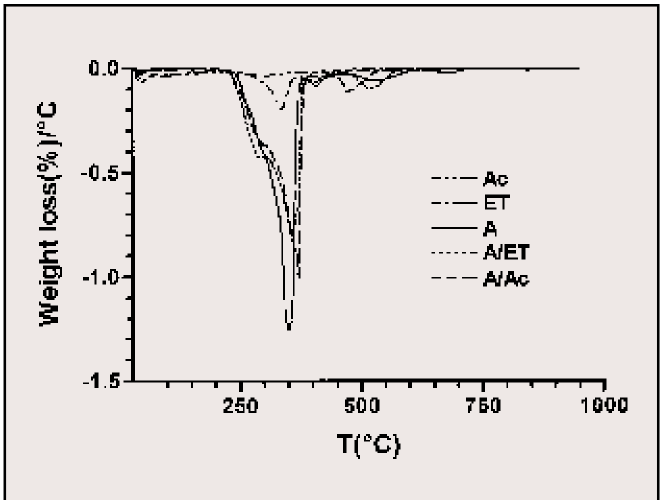

Figure 5—Differential TGA (DTGA) curves of substrates Ac and ET, and of paint A applied on glass (A), and porous substrates ET (A/ET) and Ac (A/Ac).

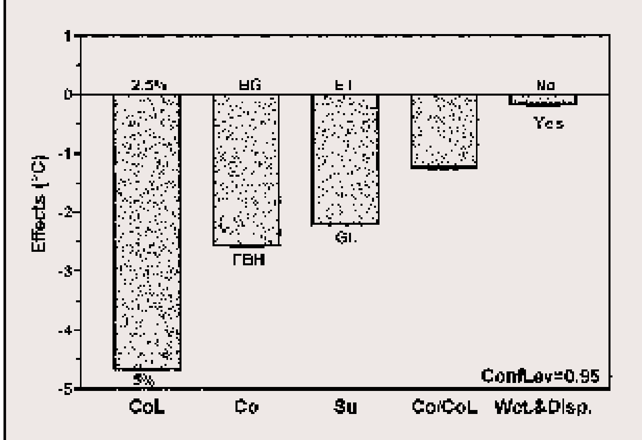

Figure 6—Mean effect of coalescent level (CoL), coalescent type (Co), substrate (Su), interaction Co/CoL, presence/absence of wetting and dispersing agents (Wet&Disp) on T_g.

actions between other coating components (dispersing and wetting agents) or between the substrate and the paint components, a (half) experimental design procedure was used. This procedure necessitated the preparation of 16 paints, two substrates (one nonporous and one porous), and 96 T_g measurements.

The analysis of the data mean effect of various parameters investigated on T_g (see *Figure* 6): (a) reconfirmed the results already described or expected, such as the fact that the higher the coalescent level the lower the T_g; the type of coalescent agent affects the Tg magnitude (for the paints investigated Lusolvan FBH has a greater plasticizing effect than butyl glycol (BG)); part of coalescent penetrates the porous substrate (ET) since the paints applied on it have higher T_g than the same paints applied on glass; for the coatings investigated the level of coalescent has a greater effect than its type, and (b) indicated that the presence/absence of wetting and dispersing agents are not statistically relevant with respect to the property measured (i.e.,T_g). This does not mean that other coating properties are not affected by these products and that they do not interact with or penetrate a porous substrate. In order to study their effect, other coating characteristics have to be considered.

CONCLUSIONS

Both the type of paint (latex) and porous substrate influence the behavior of the systems investigated. A porous substrate affects the coating characteristics because of the selective different penetration of paint components such as binder and coalescing agents. This selective penetration changes the paint composition by increasing the PVC and the MFFT of the film. The final properties of the paint film are, therefore, different from those originally expected. It follows that formulating paints, in general, and close to critical pigment volume concentration and/or having a high MFFT, in particular, should be done with care.

The thermal analysis, DSC and TGA alone or in combination with GC, once adapted to the specific conditions of the materials investigated, proved to be reliable techniques for determining the binder and the coalescing agent penetration in porous inorganic (and possibly in porous organic) substrates.

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