

Novel High-Solids Pigmented Coatings Prepared from a New-Synthesized Isophthalate-Based Oligoester, a Melamine Resin, and Various Fillers

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ABSTRACT: A new-synthesized hydroxyl-terminated isophthalate-based liquid oligoester (L-311), an hexakis(methoxymethylol)melamine resin, and various inert pigments (fillers) such as either kaolins ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) of different particle sizes (1.50 and 4.80 μm) or calcium metasilicate (CaSiO_3) were used to prepare high-solids pigmented coatings (PA and PW series, respectively). The physical, chemical, and mechanical properties (pencil hardness, Knoop hardness, flexibility, impact resistance, adhesion, gloss, solvent, and mar resistance) of the new-formulated pigmented coatings were correlated to the chemical species of the filler, the filler's load and particle size, the quantity of the crosslinker, and the introduction of large particle size colloidal silica into the coating. For measuring the mar resistance of the pigmented coatings, the Taber abrasion method was applied and the inverse wear index, $F [=I^{-1}$, cycles/cg (wear index I , weight loss (cg) per number of cycles)], was directly related to the mar resistance. Either when kaolins or calcium metasilicates were used as fillers, the Knoop hardness, the impact, and mar resistance of the films were affected from the filler's load, whereas the quantity of melamine resin (crosslinker) affected the Knoop hardness, the gloss, and the mar resistance. The fillers' particle size and the introduction of large particle colloidal silica affected mainly the mar resistance and the gloss, respectively. The pencil hardness of the PW-pigmented coatings series (F-2H) was higher than that of the PA-series (B-HB). The chemical composition of the inert pigment proved to be a very important parameter in the preparation of pigmented coatings with specific properties that aim to meet modern and particular demands for various end-up uses. All the new-formulated high-solids (nonvolatiles by weight $\sim 70\%$) pigmented coatings (PA and PW series) presented excellent adhesion (5B), flexibility ($> 32\%$), methyl ethyl ketone (MEK) resistance (>200 rubs), high pencil hardness, good Knoop hardness, and very good impact resistance (from 100 up to 160 in.-lb), independently of the species of the filler (kaolins or calcium metasilicate). © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 576–590, 2002; DOI 10.1002/app.10309

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INTRODUCTION

Over the last decade, the popularity of organic solution coatings that up to the mid-1980s were

generally supplied at approximately 50% solids by weight (nonvolatiles by weight, NVW) and were traditionally used by the manufacturers in the preparation of coatings, paints, and finishes has been seriously threatened by the growing proliferation of the VOC (volatile organic compounds) regulations imposed worldwide. Actually, nowadays this is one of the major challenges that modern coaters face and experts in the field anticipate an increased pace of the use of low-VOC coatings by the industrial finishing market. Therefore, the development of high-solids binders

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and coatings emerges as an issue of highest priority and of great technological importance.

More than any other type of commonly used binders, such as polyurethanes, epoxy and phenolic resins, acrylic resins, alkyd resins, halogenated polymers, organic silicon derivatives, and polyester resins, the latter afford a major opportunity for very low-VOC coatings, because low molecular weight oligomers can be made such that all molecules have at least two reactive groups, usually hydroxyl. Polyester resins are widely used in the paints and coatings industry because of the excellent array of properties that are obtained when the resins are crosslinked with melamine or isocyanate-based crosslinking agents.^{1,2} In particular, the versatility of redesigning the polyester backbone enables the polymer chemist to fine tune products for specific markets.

The design and development of new high-solids solvent-borne resins and coatings that can successfully meet the modern strict limitations on VOC content is our main aim. We previously studied³ the effect of the different transesterification parameters on the synthesis of high-solids liquid hydroxyl-terminated isophthalate-based oligoesters and the results obtained from that investigation led us to the preparation of a new-synthesized high-solids hydroxyl-terminated isophthalate-based oligoester, L-311, which presented enhanced processibility. In previous works, we used the L-311 for the preparation of high-solids mar-resistant clearcoats^{4,5} and talc ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$)-pigmented coatings.⁶

Pigments are insoluble, fine particle-size materials used in coatings for one or more of five reasons: (a) to provide color; (b) to hide substrates; (c) to modify the application properties of a coating; (d) to modify the performance properties of films; and/or (e) to reduce cost. Pigments are divided into four broad classes: white, color, inert, and functional pigments. Inert pigments absorb little, if any, light and have refractive indices close enough to those of binders that they give little light scattering when used as pigments. Several synonymous terms are used, such as inert pigments, inerts, fillers, and extenders, and detailed discussions of the multitude of inert pigments are available.^{7,8} Calcium carbonates, clays (aluminum silicates), mica (aluminum potassium silicates), talcs (magnesium silicates), silicon dioxides, and barites (barium sulfates) are of the most commonly used inert pigments. Although most inert pigments are inorganic minerals, organic

materials can also be used as inert pigments. For example, powdered polypropylene is insoluble and acts as an inert pigment, whereas high T_g latices, such as polystyrene latex, can be used as an inert pigment in latex paints. Commonly, but not always, inert pigments are inexpensive and reduce the cost of a coating. The principal function of most inert pigments is often to occupy volume in a film. Other functions are to adjust the rheological properties of fluid coatings; the gloss and mechanical properties of films and the volume of pigment in the film control many film properties.

In the present work, we prepared two series of pigmented coatings where the binder was L-311, the crosslinker a hexakis(methoxymethylol)melamine resin (R-747, provided by Solutia Inc.), and as inert pigment (filler), we used either kaolins ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) of different median particle diameters (mpd = 1.50 and 4.80 μm) or calcium metasilicate (CaSiO_3 , with 3.00 μm of mpd) provided by Engelhard and Nyco-Wollastonites, respectively. We focused our attention on investigating and correlating the physical, chemical, and mechanical properties [pencil hardness, Knoop hardness, flexibility, impact resistance, adhesion, methyl ethyl ketone (MEK) resistance, gloss, and mar resistance] of the new-formulated pigmented coatings to the chemical species of the filler, the filler's load and particle size, the quantity of the crosslinker, and the introduction of the large particle-size colloidal silica into the coating.

Our aim was not only to prepare pigmented coatings that could meet all the modern industrial standards regarding and implying their suitability for various end-up uses (e.g., automotive dashboards) but also to compare the film properties obtained from different fillers used in the present and previous work.⁶ In addition, we intended to find out if certain general rules that would provide useful guidelines in describing the behavior of a filler and its effects on the film properties could be extracted.

EXPERIMENTAL

Characterization Methods

FTIR spectra were obtained from a Nicolet 510P FTIR spectrometer. $^1\text{H-NMR}$ spectra were recorded by using a Bruker AC-250 spectrometer at 250 MHz. $^{13}\text{C-NMR}$ and $^{13}\text{C-DEPT}$ spectra were recorded on a Bruker AC-250 spectrometer at 60

MHz. Modulated differential scanning calorimetry (MDSC) analyses were performed with a DuPont TA 2100 thermal analyzer by using a high-temperature (600°C) cell in a N₂ atmosphere at a heating rate of 5°C/min. Gel permeation chromatography (GPC) analyses were carried out with a Hewlett–Packard 1050 series liquid chromatograph with an HP 1047A differential refractometer as detector. THF was used as a solvent at a flow rate of 0.9 mL/min through a series of three Phenogel[®] columns (pore size: 10⁵, 10³, 10² Å) and polystyrene was used for the standardization. Gas chromatography (GC) analyses were performed by using a Hewlett–Packard 5809A gas chromatograph with a flame ionization detector (FID). 1,4-Butanediol was used as internal standard and the silate agent was a mixture 80/20 v/v of hexamethyldisilazane (HMDS) and *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). The viscosities η (cP) of the pigmented coatings were determined by using a Brookfield DV-II+ viscometer at 25°C and at a spindle rate of 6 rpm (spindle #31). The nonvolatiles by weight (NVW) of the pigmented coatings were determined, upon heating at 110°C for 1 h, a sample placed in an aluminum dish in an air-circulated oven (ASTM D2369-95).

The film thickness was measured with a Microtest[®] magnetic thickness gauge and the fineness of grind of the Dispersed Products (DPOs) were measured on a Hegman gauge. The pencil hardness (PE.H) and both the direct (DIR) and the reverse (RIR) impact resistance (in.-lb) were measured according to the ASTM D-3364 and D-2794 methods, respectively. The Knoop hardness was tested on a Tukon microhardness tester (Wilson Instrument Division) and the Knoop hardness number (KHN) was determined with a load of 0.1 kg, according to the ASTM D-1474 method. The Knoop hardness number can be calculated as follows:

$$\text{KHN} = L \times (Y^2 \times C_p)^{-1}$$

where L is the load applied to the indenter (kg), Y is the measured length of indentation's long diagonal (mm), and C_p is the indenter constant (7.028×10^{-2}).

Elongation tests (ELONG) that consist of a measure of the film's flexibility and elasticity were performed on a mandrel tester according to ASTM D-522-93a method. Gloss measurements were performed by using a pocket gloss meter, the

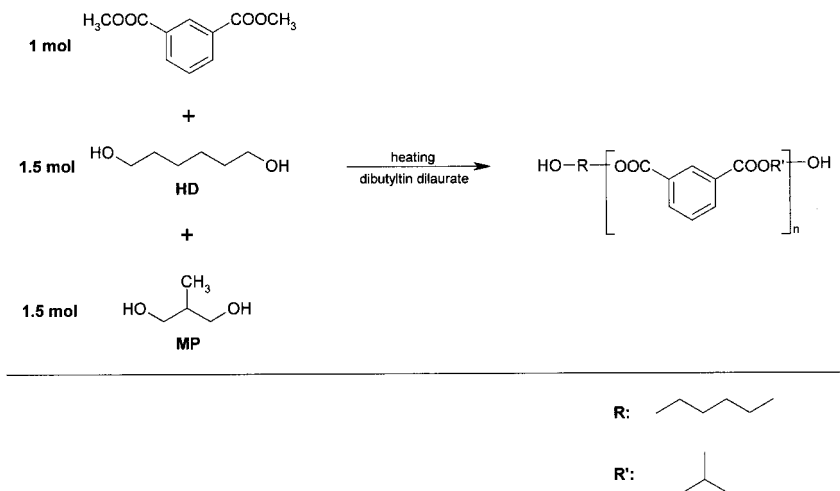
BYK-Gardner micro-TRI-gloss. MEK was tested by double rubbing with MEK-saturated unwoven paper (Kim-wipe[™]); the unwoven paper was kept saturated by MEK during the measurement. Adhesion (ADHES) was tested according to ASTM D3359-95a.

The mar resistance (M.R.) of the pigmented coatings (PA and PW series) was tested on a Taber abraser apparatus (Taber Industries) according to ASTM D-4060-90 method. More specifically, the wear index I [$(L \times 10^3)/\text{cycles}$, in cg/cycle], and the weight loss L (cg) were calculated. The mar resistance was recorded as the F ($=I^{-1}$, in cycles/cg) of the corresponding coating and was directly correlated to the F , in the following sense: The higher the F , the better the mar resistance of the pigmented coating. The abrasion test (mar resistance) was performed at 25°C and at a relative humidity of 75%. A load of 500 g on each of the pairs of the CS-17 type wheels was applied for 500 cycles.

Attempts to measure the micro-mar resistance (MMR) and microindentation hardness (MIH) of the new formulated pigmented coatings were performed by using a Digital Instruments Nanoscope III[®], scanning probe microscope, modified as previously reported.^{5,9-17} The test^{5,9-17} employed a modified scanning probe microscope (SPM) to mar the material and conventional scanning probe microscope to measure and characterize the results.^{5,9-17}

Materials

Dimethyl isophthalate (DI; 99%), 1,6-hexanediol (HD; 97%), 2-methyl-1,3-propanediol (MP; 99%), and dibutyltin dilaureate (95%) were purchased from Aldrich Chemical Co. A monomeric methyloated melamine-formaldehyde resin Resimene-747 (R-747) [hexakis(methoxymethyl)melamine (HMMM)] was obtained from Monsanto Co. (now Solutia Inc.). A fluoropolymer surface tension modifier, the Fluorad[®] (FC-430), was obtained from 3M Industrial. The Nacure-155[®] [dinonylnaphthalene disulfonic acid (DNND SA), 50 w/w % solution in isopropanol] was obtained from King Industries. The inert pigments (fillers) that we used were the kaolins (Al₂O₃·2SiO₂·2H₂O) ASP400P[®] (A480, $d = 2.63 \text{ g/cm}^3$, mpd = 4.80 μm) and ASP900[®] (A150, $d = 2.63 \text{ g/cm}^3$, mpd = 1.50 μm) provided by Engelhard, whereas the third was the calcium metasilicate (CaSiO₃) 10WOL-LASTOCOAT[®] (W300, $d = 2.90 \text{ g/cm}^3$, mpd = 3.00 μm) provided by Nyco-Wollastonites.



Scheme 1 Synthesis of the hydroxyl-terminated isophthalate-based oligoester, L-311.

Large-particle colloidal silica in ethylene glycol was provided by Nissan-Silica. Sand (1.33 mm of median particle diameter), used as a media for pigment dispersion, was purchased from Epworth Manufacturing Co. Disperbyk-182[®], used as wetting agent, was obtained from BYK-Chemie. Special Black 250[®] (furnace black of 56 nm of median particle diameter) was purchased from Degussa Co. Exxate-700[®] (provided by Exxon Chemicals) was used as solvent for the dispersion of the pigmented coatings. All materials were used as supplied.

Steel and aluminum 3 × 6 in. panels were purchased from the Q-panel Co. Steel square panels with rounded corners and with a hole (6.3 mm) centrally located in each panel as well as the abrasion wheels were provided by Taber Industries.

Synthesis of the Oligoester L-311 (see Scheme 1)

DI (582.57 g, 3.00 mol), HD (531.81 g, 4.50 mol), MP (405.54 g, 4.50 mol), and a catalytic amount of dibutyltin dilaurate (1.52 g, 0.10% w/w of total reactant weight) were placed in a round-bottom flask equipped with a Dean-Stark trap, mechanical stirrer, thermometer, N₂ inlet, and a condenser. The mixture was heated under a stream of N₂ at 200–210°C for 5 h, from the moment methanol began to collect. The transparent liquid product was quickly poured into a steel container to cool and then kept in a vial at room temperature (1305 g, yield = 98.3%, NVW = 82%, $\eta_{25^\circ\text{C}} = 2010$ cP, $d_{25^\circ\text{C}} = 1.0984$ g/cm³, VOC = 1.66 lb/gal).

$$M_n = 538, \quad M_w = 719, \quad M_p = 388,$$

$$M_z = 1016, \quad M_{z+1} = 1343,$$

$$M_v = 710, \quad D = 1.33$$

Excess of diols = 1.98% w/w

(HD, 1.49% w/w; MP, 0.49% w/w)

HO value = 355 mg KOH equiv. to 1 g sample

$$T_g = -72^\circ\text{C}$$

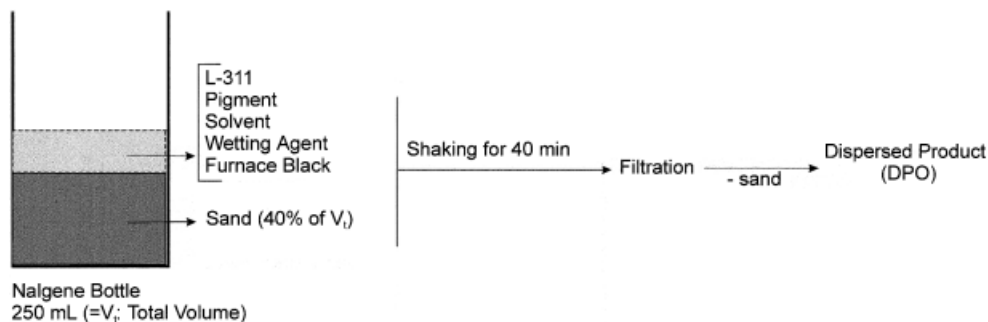
(onset temperature determined by MDSC)

FTIR, ¹H-NMR, ¹³C-NMR, and ¹³C-DEPT data of the L-311 were reported and extensively discussed in our previous work.^{3,4}

Preparation of the Pigmented Coatings

Dispersion Method (Paint Shaker)—Preparation of the Dispersed Products (DPOs)

The method selected to disperse the various fillers (kaolins or calcium metasilicate) in the L-311 was the one of the paint-shaker (see Scheme 2). We used sand of 1.30 mm median particle diameter as mill media and Exxate-700[®] as solvent. Disperbyk-182[®] was used as wetting agent and the kind of carbon black that we selected to use belonged to the category of the furnace black (56 nm median particle diameter). DPOs of 10, 20, 30, 40, and 50% v/v of A480/L-311 (A480 series) and of W300/L-311 (W300 series) as well as a DPO of 30% v/v of A150/L-311 were prepared according to the method described hereafter



Scheme 2 Schematic illustration of the paint-shaker dispersion method applied for the preparation of the various dispersed products (DPO) [quantities: sand \sim 180 g; L-311 (relative to pigment); pigment (in various v/v % on L-311); wetting agent (10 w/w % on pigment); furnace black (2 w/w % on pigment and L-311); and solvent (30 w/w % on total mixture)].

(Scheme 2). More particularly, a 250-mL nalgene bottle was charged with about 180 g of sand, filler (in various % v/v on L-311), liquid oligoester L-311 (relative to filler), Disperbyk-182[®] (10% w/w on filler), Special Black 250[®] (2% w/w on filler and L-311), and solvent Exxate-700[®] (30% w/w of the total mixture). The carefully sealed nalgene bottle was placed in a paint-shaker apparatus and shaken for 40 min. Subsequently, the mixture was filtered off and sand was removed. The dispersed product (DPO) was obtained as a black solution and kept in a vial at room temperature. The fineness of grind of all the DPOs ranged from 7^{1/2} up to 7^{3/4} of Hegman scale.

Preparation of the Pigmented Coatings (PA and PW series)

In every DPO the % w/w of the L-311 was determined separately. Subsequently, solutions of the various DPOs with the R-747 in various % weight ratios L-311/R-747 (85/15, 80/20, 75/25, 70/30, and 65/35) and FC-430 (10% w/w on total weight of the L-311, and the R-747, of a 2.5% xylene solution) were prepared at room temperature in a 50-mL beaker. Certain DPOs were also charged with large particle colloidal silica in ethylene glycol (2% w/w on total weight of L-311 and R-747). Just before application, Nacure-155[®] was mixed thoroughly into the solution, in 1.0% w/w on total weight of the oligoester and the R-747. Coatings with a thickness of 0.90–0.95 mil were prepared by casting the above solution on steel panels using a #28 draw-down rod. The panels of the PA series were baked at 120°C for 30 min and those of the PW series were baked at 160°C for 30 min. All panels were kept at ambient temperature for 1 day before testing.

For the casting of all the aforementioned solutions on the special square panels used for the abrasion tester (see Experimental), a #34 draw-down rod was used and their film thickness ranged from 1.45 to 1.50 mil.

RESULTS AND DISCUSSION

New-formulated high-solids pigmented coatings were prepared from a newly synthesized^{3,4} hydroxyl-terminated isophthalate-based liquid oligoester, the L-311 ($d = 1.10 \text{ g/cm}^3$), an hexakis(methoxymethyl)melamine resin (R-747), and various inert pigments (fillers). We experimented with the ASP400F[®] (A480, $d = 2.63 \text{ g/cm}^3$, mpd = 4.80 μm) and ASP900[®] (A150, $d = 2.63 \text{ g/cm}^3$, mpd = 1.50 μm) fillers (kaolins, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) provided by Engelhard as well as with the 10WOLLASTOCOAT[®] (W300, $d = 2.90 \text{ g/cm}^3$, mpd = 3.00 μm) filler (calcium metasilicate, CaSiO_3) provided by Nyco-Wollastonites. The abbreviations A480, A150, and W300 that we adopted in naming the three fillers represented their corresponding mpd (4.80, 1.50, and 3.00 μm , respectively) multiplied by 10.² The pigmented coatings prepared from the kaolins as fillers were named PA series and, correspondingly, those prepared from the calcium metasilicate were named PW series. When large particle colloidal silica was used in the formulations of the pigmented coatings, the abbreviation sil at the end of the name of a particular coating represented silica's introduction in the coating. Six numbers named every coating of the PA and/or the PW series after the abbreviation of their corresponding filler (A480, A150, and W300). Of the six numbers, the first

two represented the filler's load (% v/v, on L-311) and the next four the % w/w L-311/R-747 (e.g., PA480-30-7525 represented a pigmented coating where the filler was the A480, in a load of 30% v/v on L-311 and was prepared from the crosslinking of 75/25% w/w, L-311/R-747).

The applied curing conditions were 120°C for 30 min for the pigmented coatings of the PA series and 160°C for 30 min for those of the PW series. The different curing conditions were necessary because the PW-pigmented coatings series remained uncured upon curing at 120°C or even at 150°C for 30 min. This behavior could be attributed to the fact that the filler W300 has substantially higher pH (=9.9 as a 10% slurry) than A480 and A150 (pH = 3.5–5.0) do. Probably an amount of the Lewis-acid catalyst used for the crosslinking reaction (acid-catalyzed transesterification^{4,5}) of the binder (L-311) and the crosslinker (melamine resin) was consumed when the significantly basic filler W300 was used. Therefore, a higher curing temperature was applied for the crosslinking without changing the amount of the catalyst.

We focused our investigation on the correlation of the physical, chemical, and mechanical properties of the PA- and PW-pigmented coatings series to (a) the filler's load; (b) the quantity of the crosslinker (melamine resin); (c) the filler's particle size; and (d) the introduction of large particle colloidal silica into the coating. The first three variables (a, b, and c) were thoroughly investigated in a previous work,⁶ where the fillers were talcs ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot 4\text{H}_2\text{O}$) of various particle sizes (2.20, 6.63, and 10.00 μm). However, in the present work, by evaluating different fillers, we attempted to find the effect that the different chemical composition of the filler might have on the film properties and at the same time to investigate if it is possible to conclude in certain guidelines that could help in describing and anticipating certain film properties and/or curing conditions.

For measuring the mar resistance of the PA- and PW-pigmented coatings series, we applied the following three methods: (i) the crockmeter test^{4,5}; (ii) the analysis with a modified scanning probe microscope^{5,9-17}; and (iii) the Taber abra-

Table I The Properties of the Pigmented Coatings PA480-10-7030, PA480-20-7030, PA480-30-7030, PA480-40-7030, and PA480-50-7030 Prepared from Different A480 Filler Loads, 10, 20, 30, 40, and 50% v/v on L-311, Respectively

Properties	Pigmented Coatings				
	PA480-10-7030	PA480-20-7030	PA480-30-7030	PA480-40-7030	PA480-50-7030
<i>n</i> (cP)	160	165	170	175	180
NVW (%)	69	69	70	70	70
Film thickness (mil)	0.90	0.93	0.92	0.94	0.95
PE.H	HB	HB	HB	HB	HB
KHN _{0.1Kgr}	17.7	17.9	18.0	18.5	13.5
DIR (inch-lbs)	100	110	160	160	150
RIR (inch-lbs)	100	110	160	150	140
ELONG (%)	> 32	> 32	> 32	> 32	> 32
ADHES	5B	5B	5B	5B	5B
MEK (double rubs)	> 200	> 200	> 200	> 200	> 200
GLOSS					
20°	24.7	9.1	5.1	3.0	1.5
60°	71.7	51.3	39.1	28.5	17.1
85°	98.2	92.4	83.4	74.8	54.4
M.R. ^{ab}					
<i>L</i> (cg)	22.9	34.0	35.6	44.7	46.0
<i>I</i> (cg/cycle)	45.8	68.0	71.2	89.4	92.0
<i>F</i> (cycle/cg) ^c	21.8	14.7	14.0	11.1	10.9

^a The film thicknesses in Taber abrasion mar resistance test were 1.45–1.50 mil.

^b The weight loss (*L*), the wear index ($I = L^{-1}$), and the inverse wear index ($F = I^{-1}$) data were obtained from the Taber abrasion test and the inverse wear index, *F*, was recorded as mar resistance (M.R.) of the pigmented coatings.

^c The values of the inverse wear index (*F*) were multiplied by 10³.

sion test. The modified scanning probe microscopy method did not work in the case of the pigmented coatings because the surfaces were too rough⁶ to be penetrated correctly by the diamond tip and at the same time to afford reliable and reproducible results. As regards the crockmeter test, not surprisingly, we observed an increase in every angle degree of the gloss. The marring of the surface, according to the experimental procedure we had applied in the case of the clearcoats^{4,5} or even when we replaced the BonAmi[®] cleaning powder with an aluminum powder (harsher marring), resulted in the smoothing of the film's surface and subsequently to a decrease of the light scattering (higher measured gloss at a specific angle degree gloss). From all three methods, only the method of the Taber abrasion gave some reliable and repeatable results and mar resistance was recorded as the inverse wear index, $F [=I^{-1}$, cycles/cg (wear index l , weight loss (cg) per number of cycles)] (see Experimental, Characterization Methods) of the corresponding coating. Mar resistance was directly correlated to the F , in the following sense: the higher the F , the better the mar resistant of the pigmented coating.

Table I presents the properties of the PA480-series pigmented coatings (PA480-10-7030, PA480-20-7030, PA480-30-7030, PA480-40-7030, and PA480-50-7030), where the % w/w L-311/R-747 was equal to 70/30 and the A480 filler load was the only variable. Filler loads of 10, 20, 30, 40, and 50% v/v on L-311 were used. The Knoop hardness, the impact resistance, and the gloss and mar resistance were the film properties that were mainly affected from the different filler loads. The pencil hardness, the adhesion, and the flexibility remained constant. All the coatings of the specific series showed excellent adhesion (5B), MEK resistance (>200), and flexibility (>32%) and afforded films of medium pencil hardness (HB).

Figure 1 presents the changes of the KHN, DIR (direct impact resistance), mar resistance (F), and 85° gloss (G85) of the aforementioned coatings. More specifically, the coating corresponding to a load of 40% v/v of the A480 on L-311 presented the highest KHN and the one corresponding to 50% v/v showed the lowest KHN. The curve of the change of the direct impact resistance presented a peak for the PA480-30-7030 coating. It became evident that the specific coatings prepared from the A480 filler and in loads < 30% v/v on L-311 presented the worst impact resistance than their corresponding clearcoats^{4,5} and other pigmented coatings prepared in a previous work.⁶ Both the

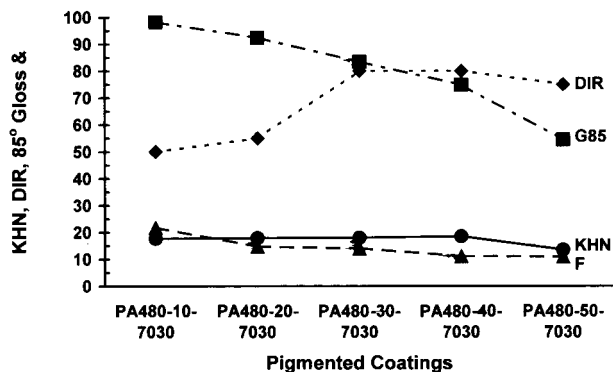


Figure 1 The changes in the KHN, 85° gloss (G85), direct impact resistance (DIR) (in.-lb), and mar resistance recorded as the inverse wear index $F (=I^{-1}$, cycles/cg) of the pigmented coatings PA480-10-7030, PA480-20-7030, PA480-30-7030, PA480-40-7030, and PA480-50-7030 prepared from different A480 filler loads, 10, 20, 30, 40, and 50% v/v on L-311, respectively. (The values of DIR are half of the original possible to create a more eloquent graph with all the presented properties.).

mar resistance (F) and the gloss (20°, 60°, and 85°) decreased as the pigment's load increased.

The properties of the PA480 series pigmented coatings (PA480-30-8515, PA480-30-8020, PA480-30-7525, PA480-30-7030, and PA480-30-6535) with 30% v/v A480/L-311, and when the quantity of the melamine resin (crosslinker coatings) was the only variable (85/15, 80/20, 75/25, 70/30, and 65/35% w/w L-311/R-747) are shown in Table II. All these coatings presented excellent adhesion (5B), impact resistance (160/160), and flexibility (>32%). The pencil hardness varied from B (for % w/w L-311/R-747 > 75/25) to HB (for % w/w L-311/R-747 < 80/20). Once more, the KHN, the gloss, and the mar resistance were the properties mostly affected by the quantity of the melamine resin.

Of these three properties, the KHN and the gloss (20°, 60°, and 85°) presented the less dramatic changes, whereas mar resistance (F) was the most intense (Fig. 2). The pigmented coating PA480-30-7030 combined enhanced film properties such as the best mar resistance and KHN and the lowest gloss values in comparison to the rest of the coatings of the specific series of the PA480 coatings.

From Figures 1 and 2, it becomes apparent that formulations consisted of 30–40% v/v load of the filler A480 on L-311 and when 65–75% w/w was the quantity of the R-747 on the total weight of the oligoester L-311 and the melamine resin

Table II The Properties of the Pigmented Coatings PA480-30-8515, PA480-30-8020, PA480-30-7525, PA480-30-7030, and PA480-30-6535 Prepared from Various % w/w L-311/R-747 (85/15, 80/20, 75/25, 70/30, and 65/35, respectively) and the Filler A480

Properties	Pigmented Coatings				
	PA480-30-8515	PA480-30-8020	PA480-30-7525	PA480-30-7030	PA480-30-6535
n (cP)	180	180	175	170	170
NVW (%)	69	69	69	70	70
Film thickness (mil)	0.92	0.93	0.92	0.92	0.94
PE.H	B	B	HB	HB	HB
KHN _{0.1Kgr}	7.3	7.5	7.9	18.0	12.8
DIR (inch-lbs)	160	160	160	160	160
RIR (inch-lbs)	160	160	160	160	160
ELONG (%)	> 32	> 32	> 32	> 32	> 32
ADHES	5B	5B	5B	5B	5B
MEK (double rubs)	> 200	> 200	> 200	> 200	> 200
GLOSS					
20°	3.3	4.4	4.5	5.1	5.3
60°	29.2	33.8	35.0	39.1	40.0
85°	73.1	73.9	74.2	83.4	84.5
M.R. ^{ab}					
L (cg)	109.5	55.9	37.0	35.6	40.4
I (cg/cycle)	219.0	111.8	74.0	71.2	80.8
F (cycle/cg) ^c	4.6	8.9	13.5	14.0	12.4

^a The film thicknesses in Taber abrasion mar resistance test were 1.45–1.50 mil.

^b The weight loss (L), the wear index ($I = L^{-1}$), and the inverse wear index, ($F = I^{-1}$) data were obtained from the Taber abrasion test and the inverse wear index, F , was recorded as mar resistance (M.R.) of the pigmented coatings.

^c The values of the inverse wear index (F) were multiplied by 10^3 .

(R-747) afforded pigmented coatings, which presented the best overall performance (e.g., low gloss, high knoop hardness, and enhanced impact and mar resistance).

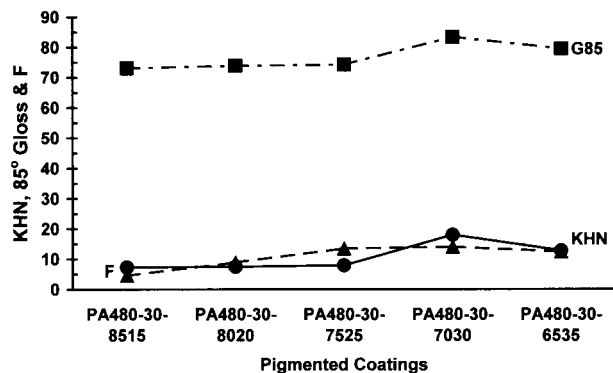


Figure 2 The changes in the KHN, 85° gloss (G85), and mar resistance recorded as the inverse wear index F ($=I^{-1}$, cycles/cg) of the pigmented coatings PA480-30-8515, PA480-30-8020, PA480-30-7525, PA480-30-7030, and PA480-30-6535 prepared from various % w/w L-311/R-747 (85/15, 80/20, 75/25, 70/30, and 65/35, respectively) and the filler A480.

The pigments A480 and A150 have a significant difference in their median particle diameters. A480 has a median particle diameter of 4.80 μm and A150 has a median particle diameter of 1.50 μm . Table III presents the film properties of the pigmented coatings PA480-30-7030 and PA150-30-7030, where the only variable was the obviously different mpd of the fillers' particle sizes.

The two coatings presented almost the same film properties except mar resistance (F). The PA480-30-7030 showed better mar resistance than the PA150-30-7030 (Fig. 3). This result came by verifying previous experimental data,⁶ where under the same experimental conditions, fillers with particles of higher median diameter and of the same chemical species contributed to higher mar resistance of the film.

We prepared formulations with the A480 and A150 filler to investigate the effect of the introduction of large particle colloidal silica (solution in ethylene glycol) 2% w/w, on total weight of the L-311 and the R-747. The film properties of the PA480-30-7030, PA480-30-7030sil, PA150-30-

Table III The Properties of the Pigmented Coatings PA150-30-7030 and PA480-30-7030 Prepared from Kaolins of Different Median Particle Diameter (1.50 and 4.80 Microns, Respectively)

Properties	Pigmented Coatings	
	PA150-30-7030	PA480-30-7030
n (cP)	160	170
NVW (%)	70	70
Film thickness (mil)	0.90	0.92
PE.H	HB	HB
KHN _{0.1Kgr}	17.8	18.0
DIR (inch-lbs)	160	160
RIR (inch-lbs)	140	160
ELONG (%)	> 32	> 32
ADHES	5B	5B
MEK (double rubs)	> 200	> 200
GLOSS		
20°	5.3	5.1
60°	40.5	39.1
85°	85.9	83.4
M.R. ^{ab}		
L (cg)	40.5	35.6
I (cg/cycle)	81.0	71.2
F (cycle/cg) ^c	12.3	14.0

^a The film thicknesses in Taber abrasion mar resistance test were 1.45–1.50 mil.

^b The weight loss (L), the wear index ($I = L^{-1}$), and the inverse wear index ($F = I^{-1}$) data were obtained from the Taber abrasion test and the inverse wear index, F , was recorded as mar resistance (M.R.) of the pigmented coatings.

^c The values of the inverse wear index (F) were multiplied by 10^3 .

7030, and PA150-30-7030sil coatings are presented in Table IV. It seemed that the introduction of small quantities of large particle colloidal silica in a pigmented coating (PA150-30-7030sil)

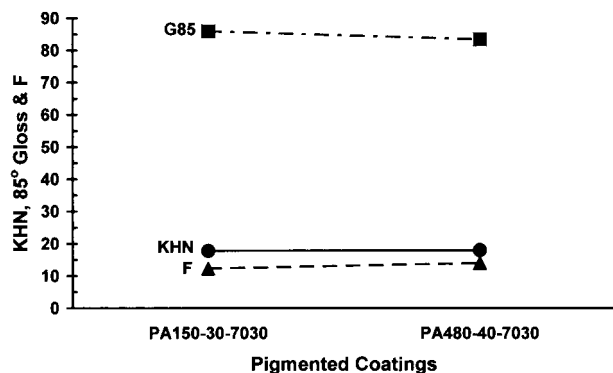


Figure 3 The changes in the KHN, 85° gloss (G85), and mar resistance recorded as the inverse wear index F ($=I^{-1}$, cycles/cg) of the pigmented coatings PA150-30-7030 and PA480-30-7030 prepared from kaolins of different median particle diameters (1.50 and 4.80 μm , respectively).

of the PA series improved dramatically the mar resistance and reduced substantially the gloss at every angle, whereas it did not affect at all the rest of the physical, chemical, and mechanical properties upon comparison to those of the corresponding pigmented coating without the colloidal silica (PA150-30-7030). The different particle size of the kaolins A480 and A150 did not differentiate the mar resistance of the pigmented coatings PA480-30-7030sil and PA150-30-7030sil because their corresponding coatings without the colloidal silica (PA480-30-7030, PA150-30-7030) presented quite the same difference in mar resistance.

Figure 4 depicts the changes of the KHN, 85° gloss, and the mar resistance (F) of the four aforementioned coatings. Not surprisingly, the percentage increase of the silica's large particles increased further the light scattering and lowered the gloss. On the other hand, the higher percentage of the hydroxyl groups of the silica seemed to benefit the mar resistance, probably because of the participation in crosslinking reactions (acid-catalyzed transesterification) with the cross-

Table IV The Properties of the Pigmented Coatings PA480-30-7030, PA480-30-7030sil, PA150-30-7030, and PA150-30-7030sil

Properties	Pigmented Coatings			
	PA480-30-7030	PA480-30-7030sil	PA150-30-7030	PA150-30-7030sil
n (cP)	170	170	160	160
NVW (%)	70	69	70	69
Film thickness (mil)	0.92	0.94	0.90	0.93
PE.H	HB	B	HB	B
KHN _{0.1Kgr}	18.0	17.3	17.8	16.9
DIR (inch-lbs)	160	160	160	160
RIR (inch-lbs)	160	160	140	140
ELONG (%)	> 32	> 32	> 32	> 32
ADHES	5B	5B	5B	5B
MEK (double rubs)	> 200	> 200	> 200	> 200
GLOSS				
20°	5.1	3.7	5.3	4.1
60°	39.1	28.7	40.5	29.1
85°	83.4	55.3	85.9	57.9
M.R. ^{ab}				
L (cg)	35.6	54.0	40.5	59.5
I (cg/cycle)	71.2	108.0	81.0	119.0
F (cycle/cg) ^c	14.0	9.2	12.3	8.4

^a The film thicknesses in Taber abrasion mar resistance test were 1.45–1.50 mil.

^b The weight loss (L), the wear index ($I = L^{-1}$), and the inverse wear index ($F = I^{-1}$) data were obtained from the Taber abrasion test and the inverse wear index, F , was recorded as mar resistance (M.R.) of the pigmented coatings.

^c The values of the inverse wear index (F) were multiplied by 10^3 .

linker (melamine resin). If such happened, a relatively more flexible crosslinked polymer network, where the long and flexible silica chains participated as well, was formed and increased the length between the crosslink sites. Also, it is a well established fact^{4–6,9,18–20} that an increased length between the melamine molecules (crosslink sites) and flexible spacers dramatically enhances the mar resistance.

Table V presents the film properties of the pigmented coatings (PW300-10-7030, PW300-20-7030, PW300-30-7030, PW300-40-7030, and PW300-50-7030) where the pigment was W300, the % w/w L-311/R-747 was equal to 70/30, and the filler's load was the only variable. Filler loads of 10, 20, 30, 40, and 50% v/v on L-311 were investigated. All the coatings of the series presented remarkable adhesion (5B), flexibility (>32%), and MEK resistance (>200), as well as very good impact resistance. The pencil hardness of these films varied from F (lower load) to 2H (higher load).

As the filler's load increased, the KHN and the mar resistance (F) increased as well, whereas the gloss at every angle, as expected,²¹ decreased

(Fig. 5). The PW300-50-7030 presented the highest Knoop hardness and mar resistance and had of the lowest gloss at every angle. The pattern of the changes of the KHN, DIR, mar resistance (F), and 85° gloss (G85) did not follow those of the pigmented coatings of the PA series (see Fig. 1). That comes to verify the significance of the filler's chemical composition that seems to play an important role in the film properties and at the same time makes extremely difficult and complex the establishment of certain rules that might describe in every detail the behavior of every commercially available filler used in coating formulations.

A series of pigmented coatings PW300 (PW300-30-8515, PW300-30-8020, PW300-30-7525, PW300-30-7030, and PW300-30-6535) with 30% v/v W300/L-311, where the quantity of the melamine resin was the only variable (85/15, 80/20, 75/25, 70/30, and 65/35% w/w L-311/R-747) prepared; their properties are presented in Table VI. These coatings presented excellent adhesion (5B), MEK resistance (>200), flexibility (>32%), and very good impact resistance (160/140 in.-lb). The films' pencil hardness was quite high (H) and was not affected by the quantity of the crosslinker.

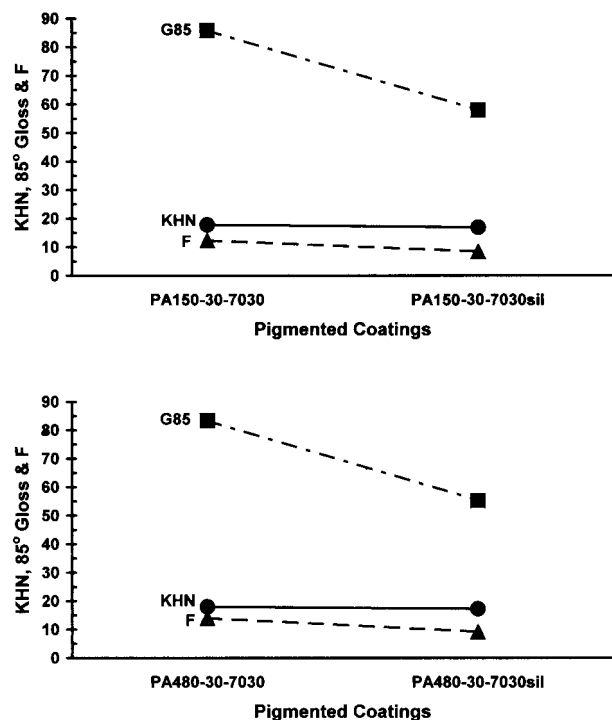


Figure 4 The changes in the KHN, 85° gloss (G85), and mar resistance recorded as the inverse wear index $F (=I^{-1}$, cycles/cg) of the pigmented coatings: (a) PA150-30-7030 and PA150-30-7030sil (top); (b) PA480-30-7030 and PA480-30-7030sil (bottom).

Figure 6 depicts the change of the KHN, 85° gloss, and mar resistance (F). The curve of the KHN presented a peak for the PW300-30-7525 coating, whereas the changes of the 85° gloss and mar resistance presented a slight increase as the percentage of the melamine resin in the formulations increased. The PW300-30-6535 presented the highest mar resistance and the PW300-30-8515 showed the lowest gloss at every angle.

Upon comparing the data from Figures 5 and 6, we may conclude that pigmented coatings prepared from formulations consisted of 40–50% v/v load of the filler PW300 on L-311 and when 65–75% w/w was the quantity of the R-747 on the total weight of the oligoester L-311 and the melamine resin (R-747) showed the best overall performance (e.g., low gloss, high Knoop hardness, and enhanced impact and mar resistance).

We also investigated the effect of the introduction of the large particle colloidal silica in PW-pigmented coatings series as we did above for the A480 and A150 fillers (see Table IV and Fig. 4). The film properties of the coatings PW300-30-7030 and PW300-30-7030sil are shown in Table VII.

The introduction of the colloidal silica resulted in a slight decrease of the gloss at every angle and the mar resistance (Fig. 7), whereas the rest of the film properties remained unaffected. The result regarding the mar resistance was the opposite of that recorded in the case of the kaolins (A480 and A150), where a dramatic increase of the mar resistance was recorded. This could be attributed to the different chemical species of the two fillers (kaolins and calcium metasilicates), a parameter that it seems should be taken under serious consideration when formulators aim to obtain the best overall performance of a pigmented coating.

The experimental data regarding the film properties of the pigmented coatings were prepared not only in this work but also in a previous investigation⁶ as well, and upon comparing to those of their corresponding clearcoats^{4,5} revealed that even though some general provisions could be made for the effect of a filler on the physical, chemical, and mechanical properties of a coating, there are no rules that could describe in detail the behavior of such filler in a coating. It seems that from all the measured film properties, the introduction of fillers in coating formulations positively affected the adhesion, whereas the pencil hardness, Knoop hardness, and gloss at every angle decreased. The mar resistance was certainly one of the properties that was also seriously affected from the introduction of the fillers, but because of the different methods that were applied to measure the mar resistance of the clearcoats (crockmeter test^{3–5} and modified SPM analysis^{4,5}) and that of the pigmented coatings (Taber abrasion method⁶), no direct relation can be extrapolated.

Upon a general evaluation of the film properties of the pigmented coatings prepared in this work, we could conclude that the calcium metasilicate (W300) afforded coatings that showed higher pencil hardness and comparable Knoop hardness, flexibility, impact resistance, adhesion, gloss, solvent, and mar resistance to those prepared from the kaolins A480 and A150. However, the mar resistance of the PW- and PA-pigmented coatings presented opposite trends.

Another very interesting result that correlates the hardness of the novel pigmented coatings, the state of the cure, and the species of the filler can be extrapolated upon comparing the significant different trends in the pencil and Knoop hardness that the PA- and PW-pigmented coatings have shown when only the amount of the filler varied

Table V The Properties of the Pigmented Coatings PW300-10-7030, PW300-20-7030, PW300-30-7030, PW300-40-7030, and PW300-50-7030 Prepared from Different W300 Filler Loads, 10, 20, 30, 40, and 50% v/v on L-311, Respectively

Properties	Pigmented Coatings				
	PW300-10-7030	PW300-20-7030	PW300-30-7030	PW300-40-7030	PW300-50-7030
n (cP)	175	180	185	190	195
NVW (%)	69	69	70	70	70
Film thickness (mil)	0.90	0.91	0.93	0.94	0.95
PE.H	F	F	H	2H	2H
KHN _{0.1Kgr}	9.6	14.0	19.0	20.3	26.2
DIR (inch-lbs)	160	160	160	160	160
RIR (inch-lbs)	160	150	140	140	140
ELONG (%)	> 32	> 32	> 32	> 32	> 32
ADHES	5B	5B	5B	5B	5B
MEK (double rubs)	> 200	> 200	> 200	> 200	> 200
GLOSS					
20°	25.1	11.6	5.9	5.3	3.8
60°	70.5	55.7	39.6	36.1	30.5
85°	96.1	87.5	78.9	75.7	69.9
M.R. ^{ab}					
L (cg)	58.8	37.2	36.5	34.1	30.7
I (cg/cycle)	117.6	74.4	73.0	68.2	61.4
F (cycle/cg) ^c	8.5	13.4	13.7	14.6	16.2

^a The film thicknesses in Taber abrasion mar resistance test were 1.45–1.50 mil.

^b The weight loss (L), the wear index ($I = L^{-1}$), and the inverse wear index ($F = I^{-1}$) data were obtained from the Taber abrasion test and the inverse wear index, F , was recorded as mar resistance (M.R.) of the pigmented coatings.

^c The values of the inverse wear index (F) were multiplied by 10^3 .

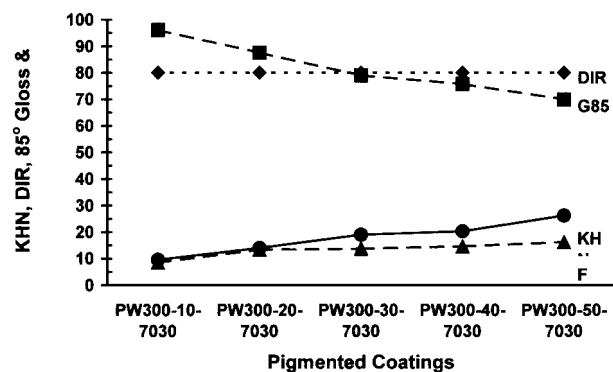


Figure 5 The changes in the KHN, 85° gloss (G85), direct impact resistance (DIR) (in.-lb), and mar resistance recorded as the inverse wear index F ($=I^{-1}$, cycles/cg) of the pigmented coatings PW300-10-7030, PW300-20-7030, PW300-30-7030, PW300-40-7030, and PW300-50-7030 prepared from different W300 filler loads, 10, 20, 30, 40, and 50% v/v on L-311, respectively. (The values of DIR are half of the original possible to create a more eloquent graph with all the presented properties.)

(see Tables I and V). Although the addition of the fillers generally increases the hardness of the polymeric materials, in the case where kaolins ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) (PA-pigmented coatings) were used as fillers, the pencil and Knoop hardness of these coatings did not follow the same trends (see Table I). The pencil hardness remained practically constant, whereas the Knoop hardness presented a slight increase for filler loads up to 40% v/v and then a decrease of 27% for a 50% v/v load. On the other hand, when calcium metasilicate (CaSiO_3) was used as filler (PW-pigmented coatings): (a) the curing temperature had to be elevated (160°C instead of 120°C applied for the PA series) for the reason we addressed here before and (b) the two aforementioned film properties related to the hardness both improved significantly as the filler's load increased (see Table V). These two different behaviors in the hardness may lead us to the assumption that the species of the filler, which is the only variable in the present case, can seriously affect the state of the cure and subsequently certain very important film properties.

Table VI The Properties of the Pigmented Coatings PW300-30-8515, PW300-30-8020, PW300-30-7525, PW300-30-7030, and PW300-30-6535 Prepared from Various % w/w L-311/R-747 (85/15, 80/20, 75/25, 70/30, and 65/35, respectively) and the Filler W300

Properties	Pigmented Coatings				
	PW300-30-8515	PW300-30-8020	PW300-30-7525	PW300-30-7030	PW300-30-6535
<i>n</i> (cP)	195	190	190	185	185
NVW (%)	69	69	69	70	70
Film thickness (mil)	0.91	0.92	0.92	0.93	0.94
PE.H	H	H	H	H	H
KHN _{0.1Kgr}	8.4	17.7	20.6	19.0	17.9
DIR (inch-lbs)	160	160	160	160	160
RIR (inch-lbs)	140	140	140	140	140
ELONG (%)	> 32	> 32	> 32	> 32	> 32
ADHES	5B	5B	5B	5B	5B
MEK (double rubs)	> 200	> 200	> 200	> 200	> 200
GLOSS					
20°	5.5	5.6	5.8	5.9	6.3
60°	33.4	34.1	35.0	39.6	41.8
85°	76.0	76.4	77.5	78.9	80.5
M.R. ^{ab}					
<i>L</i> (cg)	40.1	37.5	35.9	34.4	30.7
<i>I</i> (cg/cycle)	80.2	75.0	71.8	68.8	61.4
<i>F</i> (cycle/cg) ^c	12.4	13.3	13.9	14.5	16.3

^a The film thicknesses in Taber abrasion mar resistance test were 1.45–1.50 mil.

^b The weight loss (*L*), the wear index ($I = L^{-1}$), and the inverse wear index ($F = I^{-1}$) data were obtained from the Taber abrasion test and the inverse wear index, *F*, was recorded as mar resistance (M.R.) of the pigmented coatings.

^c The values of the inverse wear index (*F*) were multiplied by 10³.

The pigmented coating PW300-50-7030 presented the best overall performance (relatively high KHN and pencil hardness of the lowest

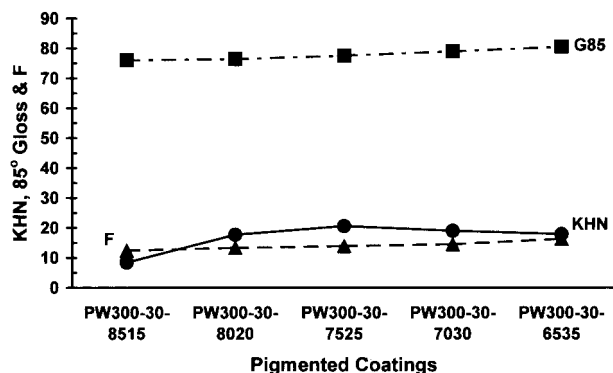


Figure 6 The changes in the KHN, 85° gloss (G85), and mar resistance recorded as the inverse wear index $F (=I^{-1}, \text{cycles/cg})$ of the pigmented coatings PW300-30-8515, PW300-30-8020, PW300-30-7525, PW300-30-7030, and PW300-30-6535 prepared from various % w/w L-311/R-747 (85/15, 80/20, 75/25, 70/30, and 65/35, respectively) and the filler W300.

gloss at every angle and good mar resistance), but it was worse than the best pigmented coating [PN633-30-7030: thickness = 0.88 mil, viscosity = 160 cP, NVW = 70%, PE.H = F, KHN_{0.1kg} = 32, DIR/RIR = 160/160 in.-lb, elongation > 32%, adhesion = 5B, MEK_{resistance} > 200 rubs, 85° gloss = 15.9, mar resistance F (cycle/cg) = 34.5] of a series of Nicron-353[®] talc (3MgO · 4SiO₂ · H₂O, Luzenac America Co.)-pigmented coatings prepared in previous work.⁶ This fact could lead us to the assumption that for the specific liquid oligoester, the L-311 and the melamine resin R-747, the filler which could afford high-solids pigmented coatings that will also combine low-gloss and enhanced mar resistance, is the talc Nicron-353[®], previously evaluated and tested.⁶

In other words, and in respect to the best film properties (low gloss, high knoop hardness and enhanced solvent, impact and mar resistance) obtained from the formulations of the high-solids liquid oligoester L-311 and the melamine resin R-747, with various fillers tested herein and also

Table VII The Properties of the Pigmented Coatings PW300-30-7030 and PW300-30-7030sil

Properties	Pigmented Coatings	
	PW300-30-7030	PW300-30-7030sil
n (cP)	185	170
NVW (%)	70	69
Film thickness (mil)	0.93	0.95
PE.H	H	H
KHN _{0.1Kgr}	19.0	20.1
DIR (inch-lbs)	160	160
RIR (inch-lbs)	140	140
ELONG (%)	> 32	> 32
ADHES	5B	5B
MEK (double rubs)	> 200	> 200
GLOSS		
20°	5.9	4.9
60°	39.6	33.9
85°	78.9	69.5
M.R. ^{ab}		
L (cg)	37.5	43.2
I (cg/cycle)	75.0	86.4
F (cycle/cg) ^c	13.3	11.6

^a The film thicknesses in Taber abrasion mar resistance test were 1.45–1.50 mil.

^b The weight loss (L), the wear index ($I = L^{-1}$), and the inverse wear index ($F = I^{-1}$) data were obtained from the Taber abrasion test and the inverse wear index, F , was recorded as mar resistance (M.R.) of the pigmented coatings.

^c The values of the inverse wear index (F) were multiplied by 10^3 .

in previous work,⁶ the Nicron-353[®] filler performed the best and the ASP400P[®] performed the worst:

Nicron-353[®] > 10WOLLASTOCOAT[®] > ASP400P[®]

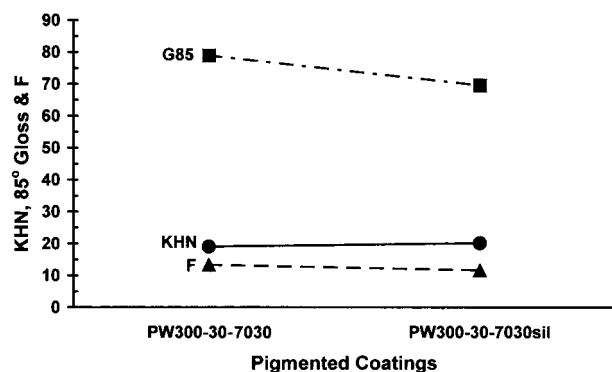


Figure 7 The changes in the KHN, 85° gloss (G85), and mar resistance recorded as the inverse wear index $F (=I^{-1}$, cycles/cg) of the pigmented coatings PW300-30-7030 and PW300-30-7030sil.

CONCLUSION

A new-synthesized hydroxyl-terminated isophthalate-based liquid oligoester (L-311), a hexakis(methoxymethylol)melamine resin, and various inert pigments (fillers) such as either kaolins ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) of different particle sizes (mpd = 1.50 and 4.80 μm) (ASP400P[®] and ASP900[®], respectively) or calcium metasilicate (CaSiO_3) (10WOLLASTOCOAT[®], mpd = 3.00 μm) were used to prepare high-solids pigmented coatings (PA and PW series, respectively).

Our investigation was focused on the correlation of the physical, chemical, and mechanical properties of the pigmented coatings (adhesion, impact resistance, pencil hardness, knoop hardness, MEK resistance, flexibility, gloss, and mar resistance) to various formulation's parameters as the pigment's load, the quantity of the crosslinker, the pigment's particle size, the introduction of large particle colloidal silica in the coating's mass, and also with the chemical composition of the inorganic pigment itself.

Of all the film properties, the pencil hardness, the impact resistance, the Knoop hardness, the gloss, and the mar resistance were those most affected from the parameters mentioned in above, in respect to both fillers used in this work.

When kaolins were used as inert pigments, the filler's load affected the impact resistance, the gloss, and the mar resistance, whereas the quantity of the melamine resin (crosslinker) affected the Knoop hardness, the gloss, and the mar resistance. The filler's particle size and the introduction of the colloidal silica affected mainly the mar resistance and the gloss, respectively.

When calcium metasilicate was used as filler (PW-coatings series), different curing conditions (160°C for 30 min) were used than those applied in the case of the kaolins (120°C for 30 min) and the quantity of the crosslinker had the same effects on the film properties as those in the case of the kaolins (see previous paragraph). The filler's load affected the Knoop hardness, the gloss, and the mar resistance. The mar resistance was also affected by the introduction of the colloidal silica but the changes of the mar resistance were the opposite of the corresponding ones in the case of the kaolins. The pencil hardness of this series of pigmented coatings (F-2H) was higher than that of the PA-pigmented coatings series (B-HB).

The PW series of pigmented coatings presented comparable film properties to those of the PA-pigmented coatings series, but the pencil hardness of the latter was substantially lower.

It became obvious that the chemical composition of the filler is another very important parameter which can determine not only the curing conditions but also the formulation rules to obtain coatings with specific end-up uses.

All the new-formulated high-solids (NVW ~ 70%) pigmented coatings (PA and PW series) independently of the filler's species (either kaolins or calcium metasilicate) used for their preparation presented excellent adhesion (5B), flexibility (>32%), MEK resistance (>200), quite high pencil hardness, good Knoop hardness, and very good impact resistance (from 100/100 to 160/160), but their mar resistance was significantly lower than that of a series of talc ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$)-pigmented coatings series previously tested.⁶

For the specific high-solids liquid isophthalate-based oligoester, L-311, and when the R-747 melamine resin is used as crosslinker, the 10WOL-LASTOCOAT[®] filler performed better than the ASP400P[®] filler, but worse than the Nicron-353[®] that was previously tested.⁶

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