In-Situ Phosphatizing Coatings II: A High-Solids Polyester Baking Enamel

Tao Yu and Chhiu-Tsu Lin—Northern Illinois University*

A single step in-situ phosphatizing coating (ISPC) can be formulated by pre-dispersing an optimal amount of in-situ phosphatizing reagents (ISPRs) into the paint system. The technique of ISPC is applied to a high-solids polyester-malemine baking enamel using a designed "ISPR-2." The in-can stability of ISPC is verified using rheological measurements. The coating properties and protective performance of the ISPC are compared to those of the multi-step coating of control sample (MCCS). The immersion tests in a 3% NaCl solution and salt spray testings show a significant improvement in paint disbondment from the "X" scribe for ISPC. The observed coating performance enhancement of ISPC over MCCS is confirmed from the multi-functionality of ISPRs. Phosphate chemistry proceeds via an acid-base type of interaction, P-O$^-$ — M^{n+}, and polymer chemistry generates a covalent P-O-C linkage with the polymer network.

INTRODUCTION

One of the key factors in determining the service performance of organic coatings is the surface characteristics of the metal to which they are applied.[1] In today's metal finishing industry, special surface pretreatment processes are usually employed to improve the substrate's acceptance of the organic coatings. Among these pre-treatments, surface phosphating conversion coating is the one most widely used for ferrous materials. Depending on the process used, surface phosphatization produces a thin layer of nonconductive amorphous iron phosphate hydrate or slightly conductive (if porous) crystalline zinc phosphate products on the steel surface. Examples of iron phosphates are $Fe_3(PO_4)_2 \bullet 8H_2O$, $FeHPO_4 \bullet H_2O$, and $FePO_4 \bullet 2H_2O$. Examples of zinc phosphates are $Zn_3PO_4 \bullet 2H_2O$, and $FeZn_2(PO_4)_2 \bullet 4H_2O$. The formation of phosphate thin film on the metal surface enhances the adhesion of the organic paint film to the substrate. By providing an electrochemical insulating iron phosphate layer (if non-porous) to the substrate surface, it also serves to inhibit the corrosion process if the organic paint film is damaged. Typically, steel substrates pass through a multi-step phosphating line, which involves alkaline cleaning, spray, or immersion phosphate conversion, and rinsing and drying procedures before organic coatings are applied on their surface.[2] The iron phosphating products thus obtained, however, usually bear a porosity of about 0.5-1.5% of the total surface area,[3] and zinc phosphates are more porous. A subsequent rinsing procedure, which traditionally utilizes highly toxic hexavalent chromate (Cr^{6+}) compounds, becomes very critical to the corrosion protective performance of the pretreated surface.[4] However, nonchrome rinses are common and are becoming more common.

Recently, a new technique of in-situ phosphatizing coating (ISPC) has been developed in our laboratory.[5,6] A successful ISPC formula can be achieved by pre-dispersing an optimal amount of in-situ phosphatizing reagents (ISPRs) into the paint system. When the coating is applied and cured on the steel surface, the ISPRs are designed to diffuse to, and react with, the metal surface to perform an in-situ phosphatization. On the other hand, the multi-functionalities of ISPRs are desirable for forming a chemical linkage to the polymer paint film. These "simultaneous" reactions of ISPRs provide the coating with covalent bonds linking to the substrate surface via the "bridge" of ISPR molecules,[7,8] and in turn, a predictable improvement in the coating adhesion. As metal phosphatizing is performed in-situ using ISPC, the process of chromate sealing is thereby avoided. Moreover, in certain cases where thick surface deposition of metal phosphate is not a strict requirement, ISPC could make possible without the utilization of a phosphating bath/line.

Presented at 24th International Waterborne, High-Solids, and Powder Coatings Symposium, February 5-7, 1997, New Orleans, LA.

*Dept. of Chemistry and Biochemistry, DeKalb, IL 60115-2862.

Table 1—Glass Transition Temperature for MCCS and ISPC

Sample	T_{gonset} (°C)	$T_{goffset}$ (°C)	T_{gspan} (°C)	T_g (°C)	ΔC_p(mJ/mg•°C)
Clear MCCS[a]	-76.7	-56	20.7	-66.5	0.582
Clear ISPC[b]	-74.5	-52.3	22.2	-63.3	0.572
Clear MCCS[c]	37.1	60.1	23	48.6	0.346
Clear ISPC[c]	34.4	68.2	33.8	51.3	0.322
Pigmented MCCS[c]	17.3	40.6	23.3	28.9	0.088
Pigmented ISPC[c]	20.6	44	23.4	32.5	0.085

(a) Coating sample before baking procedure.
(b) Coating sample before baking, after eight weeks of storage at room temperature.
(c) Coating samples after curing procedure.

In our previous publications,[7,9,10] we reported in detail the chemical affinities of ISPRs and the phosphating chemistry of ISPC on cold-rolled steel (CRS) substrates. The successful formation of iron phosphate product on the CRS surface using ISPC is also carefully characterized. Following studies of a simplified formula for solventborne polyester ISPC model paint,[10] we are now applying the ISPC technique to a high-solids polyester-melamine baking enamel formula on the basis of a marketable control paint product. In this paper, the corrosion protection performance of ISPC will be reported in comparison to the corresponding multi-step control coating sample (MCCS), which uses the original high-solids formula. Successful phosphatization using our ISPC formula will be verified, and the ISPR related effects on the coating's polymer chemistry and its storage stability will also be examined.

EXPERIMENTAL

High-solids polyester-melamine baking enamel paint samples were supplied by The Sherwin-Williams Company. The MCCS control formula selected is a gloss ivory paint (Permaclad® 2500) with a solids content of 82.4% as determined by ASTM D 2369-90 (NVM bake of 60 min at 110°C), converting to 3.00 lb/gal paint VOC. A modified formula of the high-solids clear (unpigmented) version (Permaclad® 2523) of this particular control coating is used for polymer chemistry studies. The unpigmented coating has a solid content of 74.0% as measured using the same method. This high-solids MCCS formula is then modified to form an ISPC formulation using a designed in-situ phosphatizing reagent, "ISPR-2" (an aryl phosphonic or phosphoric acid, see reference (11) for the detailed formulation). The amount of ISPRs used is usually within the range of 0.5-5% to the weight of the complete formula. ISPC and MCCS are sprayed, respectively, on standard testing panels and cured 15 min at 163°C (for all specimens unless mentioned otherwise) to obtain a dry film thickness of about 25.4 μm (1.0 mil). Three types of steel testing panels were acquired from ACT Laboratories Inc. to be used as substrates: (1) clean, unpolished bare CRS panels, (2) B-1000 iron phosphated panels with only deionized (DI) water rinse, and (3) B-1000 iron phosphated panels with P60 (Parcolene 60 standard chromate) passivating.

A differential scanning calorimeter, a Seiko DSC 220C model (Seiko Scientific Instruments), is employed for the thermal analysis of the coating films cured under the previous conditions on CRS panels. The baked paint films are peeled mechanically from the substrate for glass transition temperature (T_g) measurement. Prior to actual DSC scanning, all samples are annealed in the DSC oven for one minute at 100°C to release the stress resulting from the mechanical peeling and sampling of the polymer coating film. This temperature is chosen to be above the T_g expected for completely cured coating films and well below the coating's curing temperature. The calorimeter is equipped with a Seiko SSC5200H Disk Station for scanning and annealing program manipulations and data analysis. DSC scanning is conducted from -100° to 100°C at a heating rate of 10°C/min.

In electrochemical impedance spectroscopy (EIS) measurements, ac impedance data are acquired at the open-circuit potential using a PARC 273 potentiostat/galvanostat (EG&G Princeton Applied Research Corp.) and a PARC 5210 lock-in amplifier. The working electrode formed by the paint coated steel panel has an exposure area of 10.0 cm^2 to the 3% NaCl cell solution. This area is pre-soaked in the same solution for 72 hr before EIS evaluations are taken. The EIS measurement programming control, data acquisition, and analysis are conducted using an electrochemical impedance software, EG&G Model 398 (EG&G Instruments Corp.). In all cases, the impedance measurements are carried out over the frequency range of 100 KHz to 10 mHz. Similar apparatus are utilized for cathodic delamination tests. Here a 20.0 cm^2 area of the working electrode is exposed to the cell solution, and the working electrode is polarized to –1100 mV versus the saturated calomel electrode (SCE) throughout all testing periods. The dynamic potential control and delamination current data acquisition are carried out utilizing an EG&G corrosion measurement software Model 342C.

Reflectance FTIR measurements are conducted using a Bruker FTIR spectrophotometer model Vector 22 equipped with a Spectra Tech FT-80 grazing angle accessory. The ISPC formula is applied and cured on CRS panels. Before the ISPC formula is applied and cured on metal surface, the CRS substrates used for FTIR measurements are mechanically polished to give a 0.05 μm diamond finish. The substrate surfaces are subjected to the reflectance FTIR measurements after the cured polymeric topcoatings being removed by solvent stripping without damaging the in-situ phosphating products.[9] The transmittance spectrum of this metal phosphate thin film is recorded by ratioing the resulting single-beam spectrum with that obtained from the same substrate surface before coating application. The interferometer is

purged with dry nitrogen. Water, carbon dioxide, and baseline corrections are necessary in most cases.

Paint rheology is monitored by a Brookfield cone/plate viscometer, a RVDV-IIICP model (Brookfield Engineering Laboratories, Inc.) equipped with a CP-52 cone spindle (24 mm diameter, 3.0° cone angle). Shear rate control programming, data acquisition, and processing are conducted by using a Brookfield Rheocalc software, version 1.4. All rheological measurements are taken at the fixed temperature of 25.0 ± 0.1°C.

RESULTS AND DISCUSSION

Crosslinking Density Verification for the Coatings

For surface protective organic coatings, the barrier mechanism is one of the principal means by which corrosion resistance performance is achieved. This mechanism takes effect by lowering the coating's permeability to corrosive agents through the polymeric or pigmented polymer composite coating film, and by enhancing the coating's resistance against the so-called "water disbondment."[12] Because of this process, any corrosion protection property comparison between two coating systems has to be made on coating films with very similar crosslinking status of their polymer network. For polyester-melamine baking systems, the film forming crosslinking is realized in the presence of acid catalysts. In ISPC formulas, the ISPRs typically used also bear various degrees of acidity as a requirement from phosphate chemistry, which we have previously clarified.[7] Based on the concern that ISPRs might act as an additional acid catalyst for the film-forming polymerizations, a crosslinking density adjustment becomes a necessity for appropriate property comparison.[13] For both clear and pigmented formulas under study, roughly similar crosslinking density in the high-solids ISPC to that of MCCS is assured by monitoring the glass transitions of the cured coating film. The determination of T_g and the heat capacity change (ΔC_p) during the transition is completed by using a differential scanning calorimeter (DSC).

In linear polymers, T_g value is directly related to the molecular weight (MW) of specific polymer molecule (up to a certain chain length). Direct relationships between T_g value and polymer crosslinking density is very complicated and, in general, is strongly dependent on the structural detail of the polymer system involved. A detailed review of the subject[14] derives from the free volume concept, suggesting a linear relationship of T_g to crosslinking density for a specific polymer system (assuming that the degradation, self-condensation of crosslinkers, and other processes are absent). The T_g span is the temperature difference between the onset and offset temperatures of the glass transition, i.e., the temperature region covering the entire glass transition state. Another change of thermodynamic value coupling with the glass transition is the heat capacity (C_p). The difference in heat capacity of polymers in liquid (or elastic) state and glassy state, i.e., $\Delta C_{p(Tg)} = C_{p(l)} - C_{p(g)}$, decreases steadily as the crosslinking density develops. The works done by Mathot[15] and by Montserrat[16] illustrate roughly a linear relationship between $\Delta C_{p(Tg)}$ and the reciprocal of T_g.

The DSC measurements of T_g, T_g span, and ΔC_p for the unbaked and cured clear, and cured pigmented ISPC and MCCS coatings are listed in *Table* 1. The data listed in the first two rows in *Table* 1 concern the unbaked paints and will be discussed later. The general observations in *Table* 1 are: (1) for the unpigmented paint, a slightly higher T_g value is observed in the ISPC formula (these T_g values are reproducible), suggesting a higher degree of network crosslinking. This is further supported by a smaller value of $\Delta C_{p(Tg)}$, corresponding to a slimmer free volume release during glass transition in a more tightly compacted polymer paint film. This enhancement in the polymer curing is probably due to the acidity of ISPRs in the formula, which imparts the catalysis of major film forming reactions.[13] Both clear MCCS and ISPC cured films have a pencil hardness of F, but ISPC gives a slightly brittle film. The T_g span for the ISPC formula is expended to some extent, indicating the existence of a wider range of dispersion of crosslinking density throughout the cured film. In terms of coating property, improving the degree of curing means a harder but possibly more brittle film. A larger distribution in the degree of crosslinking compensates for this possible introduction of more brittleness by providing more flexible fractions which have less crosslinking; (2) for the pigmented high-solids formula, this limited trend of ISPR enhanced polymer curing in ISPC is maintained. The pencil hardness of pigmented MCCS and ISPC was measured as 4H and 5H, respectively; and (3) for commercial organic coatings, the incorporation of pigments and fillers usually raises T_g value. In *Table* 1, a lowered T_g value and a significantly suppressed $\Delta C_{p(Tg)}$ for the pigmented formula are recorded as compared to those of clear paint. The exact reason for the observation of lower T_gs with the pigmented formulas is not known, but it seems to follow some highly filled polymer composite systems,[17] where the mobility of polymer molecules has been hindered by the large volume of pigments. Overall, the cured coating films of ISPC and MCCS have similar T_g values and pencil hardness qualities. Thus, the control and modified coatings should be similar enough for comparisons to be made.

ISPC Corrosion Resistance Measurements

Recently, electrochemical impedance spectroscopy (EIS) has been used in coating evaluations.[18] EIS provides a rapid, nondestructive means for characterizing not only the corrosion rate, but also the corrosion mechanism of metals in a variety of environments. There are reports that the EIS method is used to evaluate the quality of industrial phosphate conversions on bare metal surfaces,[19] as well as on phosphated steel surfaces with an organic topcoating.[20] In our laboratory, the EIS method is also used for the evaluation of paint film dielectrics and corrosion protective behavior of metal phosphate interface between coating and substrate.[21] In this pigmented high-solids ISPC coating, the corrosion resistance performance is predicted also by EIS measurements, and results are compared to the corresponding pigmented MCCS formula. Measurements are made for

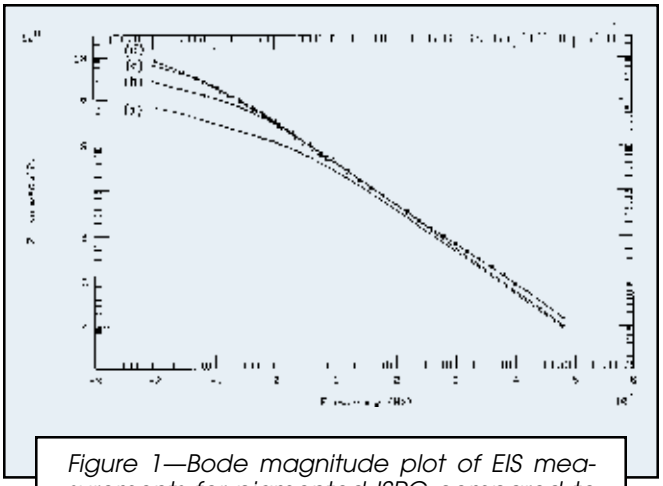

Figure 1—Bode magnitude plot of EIS measurements for pigmented ISPC compared to MCCS: MCCS on bare CRS panel (a) and on B-1000 pre-phosphated panel (b); ISPC on bare CRS panel (c) and on B-1000 panel (d).

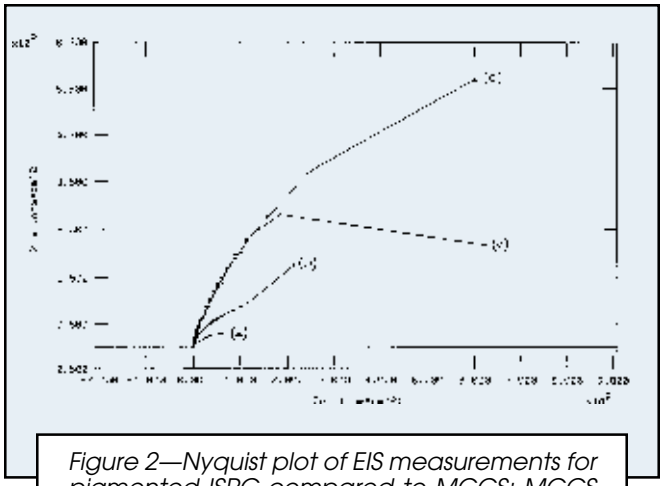

Figure 2—Nyquist plot of EIS measurements for pigmented ISPC compared to MCCS: MCCS on bare CRS panel (a) and on B-1000 pre-phosphated panel (b); ISPC on bare CRS panel (c) and on B-1000 panel (d).

coatings applied and cured on bare CRS and iron phosphated B-1000 panels (with only DI water rinse) separately. The EIS results are shown in the Bode plot (*Figure* 1) and Nyquist plot (*Figure* 2), two representative reporting formats for EIS measurements. A detailed review is given by Walter[22] on the analysis of EIS data by using such plotting methods for corrosion performance prediction of the painted steel coupons. The impedance values at the low frequency end of 10 mHz are reported as follows: $|Z| = 6.6 \times 10^9\ \Omega \bullet cm^2$ for ISPC on bare CRS and $8.3 \times 10^9\ \Omega \bullet cm^2$ on B-1000 panel, $|Z| = 6.9 \times 10^8\ \Omega \bullet cm^2$ for MCCS on CRS, and $2.8 \times 10^9\ \Omega \bullet cm^2$ on B-1000 substrate.

Two major factors determine the overall impedance of the coated steel surface being measured: the dielectric properties related to the cured coating film itself, and that related to its interface with the metal substrate. The latter is especially important providing the existence of an insulating interfacial metal phosphate thin film. Those are the cases when MCCS is applied on prephosphated panels, or ISPC is used to give in-situ phosphating products. While the coating films of pigmented MCCS and ISPC have almost identical chemical formations and bear similar crosslinking densities, we expect differences in the coating's impedance response to stem mostly from the interfacial property change, i.e., the contribution from the phosphating products. From the Bode plot results (*Figure* 1) it is apparent that MCCS applied on iron phosphated B-1000 panel (curve 1a) has an enhanced impedance value in contrast to that on bare CRS (curve 1b). This is readily understandable when one considers contributions from the insulating products of surface phosphating pretreatment. Using ISPC, on the other hand, results in even higher impedance values for the overall coating (curves 1c and 1d as compared to curves 1a and 1b), and the differences made by substrate pretreatment almost extinguishes (curves 1c and 1d). The superimposable results of ISPC on CRS (curve 1c) and on B-1000 (curve 1d) panels indicate a comparable corrosion resistance performance of the two, suggesting a similar insulating nature of ISPC phosphating products to that resulting from standard iron phosphate pretreatment. Comparing the results of ISPC on CRS (curve 1b) and MCCS on B-1000 (curve 1c), a better coating performance from ISPC is clearly observed. The result reflects quite well with the designed chemical principle of ISPC where ISPR forms metal phosphate layer, links covalently with polymer resin, and catalyzes selectively the polymer chemistry. A similar picture is given by the Nyquist plot (*Figure* 2), in which impedance is revealed by the diameter of the semicircle fitting of the data points. From the resulting diameters of semicircle fitting, the impedance for the testing coatings is determined as: $|Z| = 8.5 \times 10^9\ \Omega \bullet cm^2$ for ISPC on CRS and $1.4 \times 10^{10}\ \Omega \bullet cm^2$ on B-1000 panel, $8.5 \times 10^8\ \Omega \bullet cm^2$ for MCCS on CRS and $2.1 \times 10^9\ \Omega \bullet cm^2$ on B-1000. The impedance improvements from substrate surface pretreatment, and from ISPC, are obvious. Moreover, in ISPC applications, differences made by the substrates are better resolved here. This divergence can be seen from the later splitting of curves 2c and 2d, and the different diameters resulted from the semicircle fitting. It is well known that standard pretreatment results in a phosphate product with a somewhat porous surface, if no sealing procedure is involved. The B-1000 panels used here are with DI water rinse only, which are exactly of this type. The higher impedance result for ISPC on such panels suggests that the ISPRs may be able to take additional phosphating effects at those "defective" spots to give a more perfect insulating thin film.

While EIS gives a favorable result for the high-solids formula of ISPC in suggesting a comparable, maybe even improved, corrosion resistance to MCCS over standard pretreatment, it requires further verifications by standard corrosion tests. The results for the salt water immersion test and the salt spray tests are presented in *Figures* 3 and 4, respectively. The actual measurements of paint disbondment from the "X" scribe after 144 hr (as called for by the spec of MCCS over B-1000) in salt water immersion and salt spray tests are listed in *Table* 2.

From the data listed in *Table* 2, it is obvious that the ISPC formula does show improved corrosion resistance

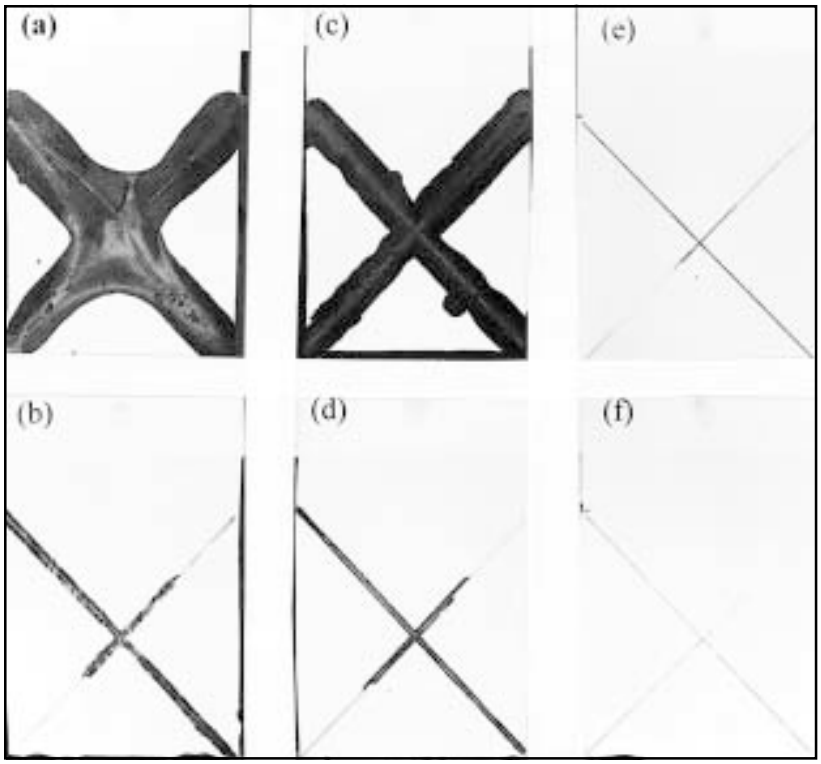

Figure 3—Comparison of testing panel appearance after 144 hr of exposure in salt water test: MCCS pigmented formula coated on bare CRS panel (a), B-1000 pre-phosphated panel (c), and the bonderized panel with P60 chromate rinse (e); ISPC pigmented formula coated on bare CRS panel (b), B-1000 pre-phosphated panel (d), and the bonderized panel with P60 chromate rinse (f).

performance compared to that of MCCS applied on the same substrate. MCCS applied on a bonderized B-1000 panel is actually representative of the current multi-step processes. Compared to that of MCCS on B-1000, better performance in water immersion is achieved for ISPC applied on bare CRS testing coupons. This result is consistent with our predictions from the EIS data. Furthermore, salt spray results show a comparable performance of ISPC on B-1000 panels with DI water rinse, to that of MCCS applied on phosphated coupons with Parcolene 60 chromate rinse. This supports our suggestion that, even on pre-phosphated substrates, using ISPC can possibly improve the pore sealing and give a better surface phosphatization. This conclusion makes the technique of ISPC a possible alternative for the environmentally unfriendly chromate post-treatment procedures.

The origin of these improvements in the corrosion protection of ISPC lies in the in-situ phosphatization being performed by the ISPRs in the coating formula. Characterizations of the interfacial metal phosphate product have been detailed in our previous publications.[9,10] In this specific high-solids ISPC formula, the effectiveness of the in-situ phosphatization is verified by using reflectance FTIR technique. FTIR results are shown for the use of both clear (*Figure* 5a) and pigmented (*Figure* 5b) ISPC coatings on CRS. It has been established that phosphate chemistry produces an acid-base type interaction of $P\text{-}O^{-}—M^{n+}$ in reacting with the metal substrate. From both spectra, the formation of metal phosphate product is proved by the peaks at 1073 and 574 cm^{-1}, corresponding respectively to the υ_3 and υ_4 vibrational mode of the phosphate group being distorted by the crystal field. For the two spectra obtained from clear and pigmented coating systems, the observable differences in the peak shape and intensity stem from the fact that ISPRs are designed to diffuse to the metal surface during the curing procedure to take their effect. The mechanism is obviously controlled by the diffusibility of ISPRs in the two systems which have different viscosities. Besides phosphatization, ISPRs in the formula have the function of reacting with backbone polymers in the coating to form covalent bond linkage with the polymer. This is confirmed spectroscopically by the peak around 944 cm^{-1} in both

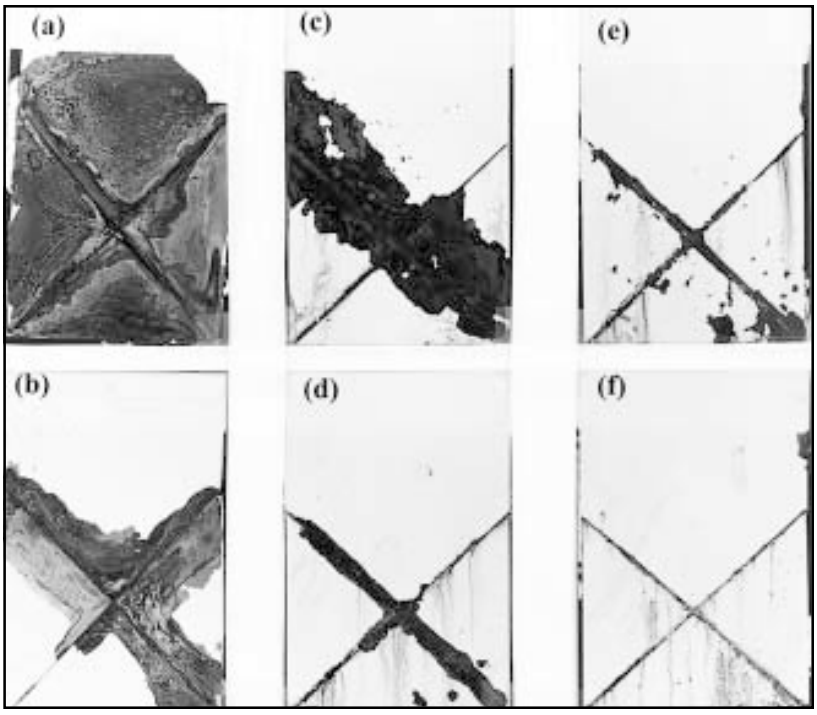

Figure 4—Comparison of testing panel appearance after 144 hr of exposure in the salt spray test (ASTM B 117): MCCS pigmented formula coated on bare CRS panel (a), B-1000 pre-phosphated panel (c), and the bonderized panel with P60 chromate rinse (e); ISPC pigmented formula coated on the bare CRS panel (b), B-1000 pre-phosphated panel (d), and the bonderized panel with P60 chromate rinse (f).

Table 2—Disbondment from "X" Scribe in Salt Water Immersion and Salt Spray

Samples	Salt Water Immersion (mm)	Salt Spray (mm)
MCCS on bare CRS	22	Complete failure
ISPC on bare CRS	5	28-40
MCCS on B-1000 (DI rinse only)	15	35
ISPC on B-1000 (DI rinse only)	3	8
MCCS on B-1000 (P60 chromate rinse)	1.0	5
ISPC on B-1000 (P60 chromate rinse)	<0.5	2

spectra, corresponding to the P-O bond being distorted by the P-O-C linkage formed.

These ISPR reactions give the coating an advanced chemical bonding attachment to the substrate surface. This, in turn, should provide the ISPC coating with improved adhesion properties. The adhesion of organic coatings on a metal substrate can be evaluated with tape test (ASTM D 3359) and cathodic delamination. The results of dry adhesion test on bare CRS substrate using cross-hatched pattern and a pressure sensitive tape (3M Corp.) are 2B and 3B for clear MCCS and ISPC, respectively; and 5B for both pigmented MCCS and ISPC. The wet adhesion disbondment from "X" scribe after 144 hr of salt water immersion followed by applying a 3M adhesive tape is displayed in *Figure* 3 and listed in the second column of *Table* 2. The results may be classified as 0A and 2A for pigmented MCCS and ISPC on bare CRS, respectively; 1A and 3A for pigmented MCCS and ISPC on iron phosphated B-1000 (DI rinse only), respectively; and 4A and 5A for pigmented MCCS and ISPC on iron phosphate B-1000 (P60 chromate rinse), respectively. The adhesion of coating films to metallic substrates can also be assessed by an electrochemical process which accelerates the coating's delamination by applying certain voltage to the teting panel as the cathodic working electrode.[23] The coating disbondment area development during cathodic delamination of the pigmented high-solids ISPC formula is plotted as curve 6a in *Figure* 6, as compared to that of MCCS (curve 6b) on the same substrate of bare CRS. The results prove the noticeable reduction of disbonding rate for ISPC starting from as early as 12 hours of the experiment. This difference is well maintained throughout the delamination process.

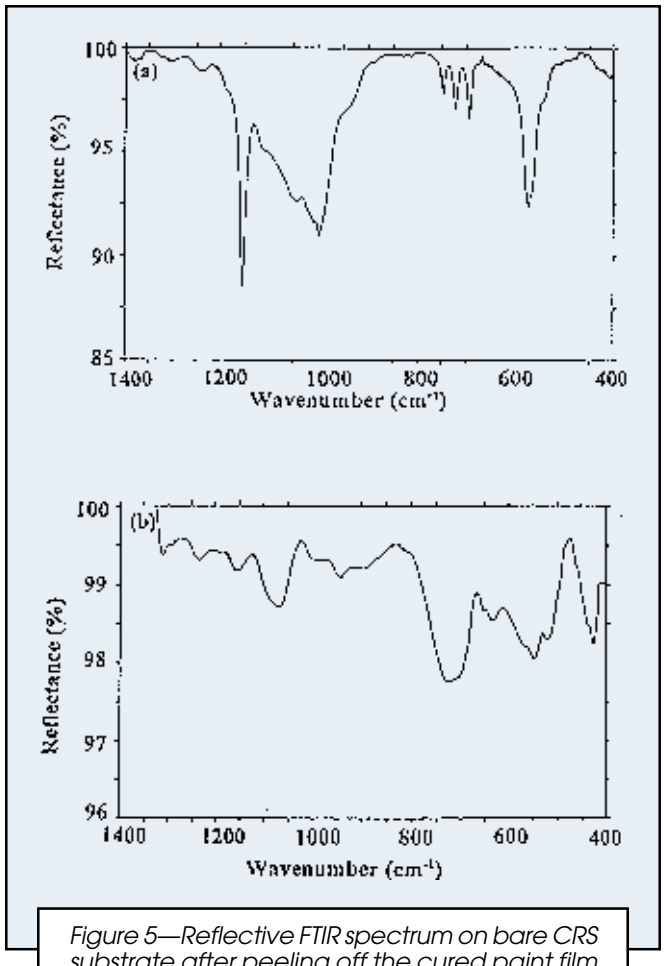

Figure 5—Reflective FTIR spectrum on bare CRS substrate after peeling off the cured paint film of ISPC clear (a) and pigmented (b) high-solids formula.

Storage Stability of ISPC and Its Polymer Chemistry

It is well known that the main film forming crosslinking reaction in polyester-melamine baking enamels is strongly acid catalyzed.[24] While the ISPRs that we use usually bear some acidity, concerns about the storage stability of the ISPC need to be evaluated, even though crosslinking reactions are believed to be negligibly slow at room temperature. Evaluation is done by monitoring the rheological behavior of both clear (*Figure* 7) and pigmented (*Figure* 8) ISPC formulas during room temperature storage. The viscosities at the various storage times (corresponding to *Figure* 7) are measured as 494 cp for the control MCCS formula; and 738 cp (freshly prepared), 870 cp (one-week storage); 1036 cp (two-weeks storage); 1171 cp (three-weeks storage), 1389 cp

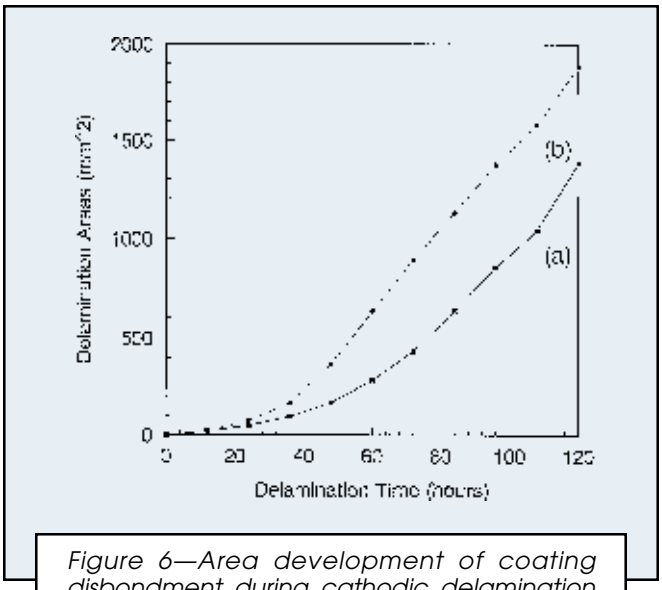

Figure 6—Area development of coating disbondment during cathodic delamination evaluations: pigmented ISPC formula (a) and pigmented MCCS (b) on bare CRS substrates.

(four- weeks storage), 1530 cp (five-weeks storage), and 1870 cp (10-weeks storage) for the modified ISPC formula.

Without influence from pigments, the rheological responses of the clear ISPC formula are dominated by the behavior of polymer molecules in the system. All curves in *Figure* 7 are representative of typical Newtonian flow properties, as shown by the perfect linear shear stress-shear rate relationship and the excellent overlapping of the "up and down" scanning curve. Also, from the different slopes of the curve, it is noticeable that the freshly prepared ISPC formula leads to an initial increase in the paint viscosity to 738 from 494 cp of the control MCCS formula. This viscosity increase shows clearly a trend to slow down within the first eight weeks after sample preparation (curves 7b to 7e). It is imagined that the viscosity will eventually stabilize at a point with slightly higher absolute value, i.e., 1870 cp in 10-weeks storage at room temperature. It should be noted that the clear ISPC system aged for 10 weeks is perfectly sprayable by the JGV™ suction feed spray gun without the addition of solvents. The rheology characteristic of the coating, i.e., a perfect Newtonian flow, remains unchanged throughout the evaluation process. Similar conclusions can be derived from the rheology responses of the pigmented ISPC formula, except that the pigmented paint shows a shear thinning behavior, i.e., the paint sample exhibits lower viscosity under higher shear rate. The lower viscosities reflected in the backward scanning (where shear rate decreases from a higher value) following the forward scanning (where shear rate increases from a lower value) are clearly affected by the coating's shear history. *Figure* 8 shows a log-log plot of absolute viscosity (η) and shear rate.[25] Although an initial viscosity increase is also observed, the apparent overlapping of the curves (curves 8c to 8e) for ISPC after two weeks of aging supports the prediction that the trend is decreasing. The shortened stabilizing time in this pigmented system is owed again to the restrictions on polymer molecular mobility made by the large volume of pigments in the formula. Compared to that of MCCS, it is also observable from the curves that the ISPC formula shows slightly less shear thinning. The degree of the paint shear thinning effect can be reflected by the area surrounded by the "up and down" scanning curves. But in all cases, the coating maintains its rheology characteristic as a non-Newtonian flow. The pigmented ISPC system aged for four to eight weeks is also perfectly sprayable without additional solvents reduction.

As the initial viscosity increase is clearly seen in the clear ISPC formula, it is reasonable to suggest that the polymer chemistry is affected by the existence of acidic ISPRs in the system. At least two possible chemical origins of the polymer chemistry are possible: (1) a low level polymer crosslinking triggered by the ISPRs during room temperature storage, and (2) some degree of polymer chain extension resulted from a transetherification reaction involving the resin OH groups and the melamine.[24] Reactions of the type (1) could lead to the emergence of some three-dimensional crosslinked microgels in the coating system. Some reports show that even a very small fraction of microgels with quite slight crosslinking could affect the rheology

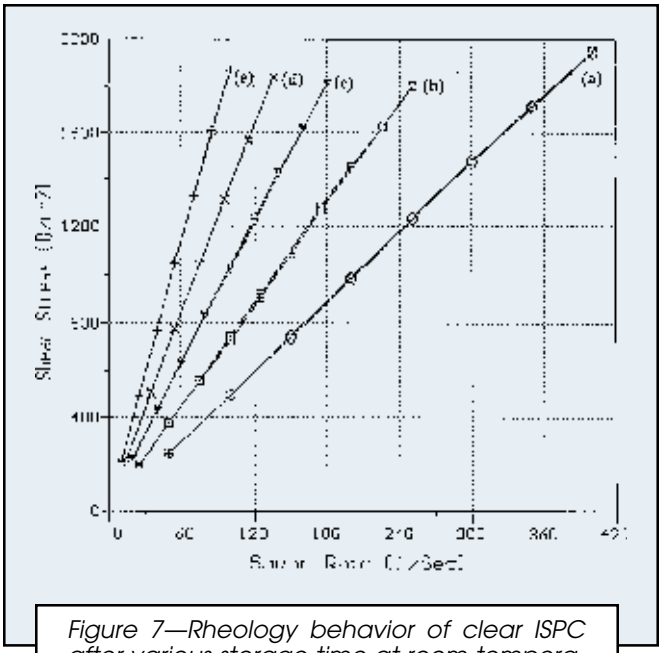

Figure 7—Rheology behavior of clear ISPC after various storage time at room temperature: MCCS control (a); ISPC formula after one week (b), two weeks (c), four weeks (d), and eight weeks (e) of storage.

property of a polymer solution by changing it from perfectly Newtonian to shear thinning in the moderate shear rate and shear stress range.[26] In the present case, the clear ISPC remains perfectly Newtonian, so that the possibility of room temperature crosslinking development is not supported. A further proof of this conclusion comes from the thermal analysis on the unbaked sample of clear ISPC after eight-weeks storage, which shows the

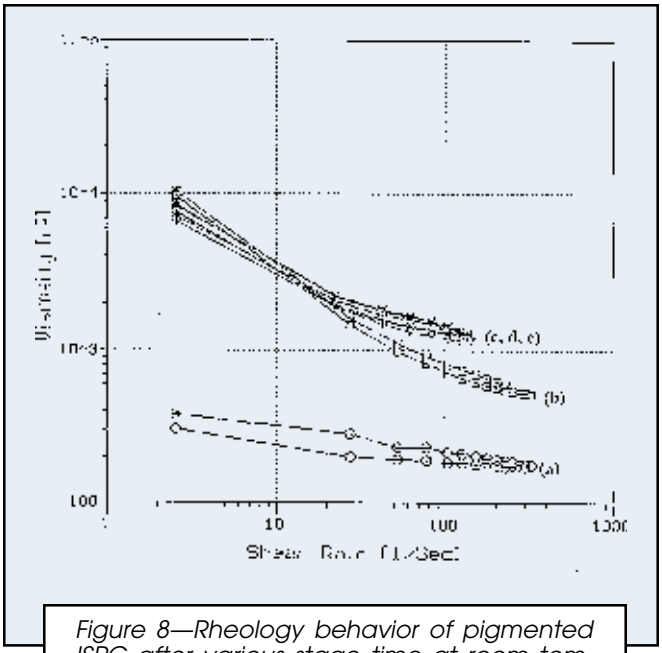

Figure 8—Rheology behavior of pigmented ISPC after various stage time at room temperature: MCCS control (a); ISPC formula after one week (b), two weeks (c), four weeks (d), and eight weeks (e) of storage.

highest absolute viscosity value (about 1870 cp). The DSC scanning results of the unbaked ISPC paint, compared to that of MCCS, are listed in the first two rows in *Table* 1. The results show a minor upward T_g shifting for ISPC coupled with a very slight decrease in the $\Delta C_{p(Tg)}$, suggesting that the ISPR assisted crosslinking at room temperature is unimportant. Observing the increase in T_g span for this specific ISPC sample, which implies a sufficient chain extension of linear polyester MW distribution, it may be a more reasonable suggestion that the acidic ISPRs are catalyzing the self-condensation of the polyester molecules. A slight upward shift of both onset and offset temperatures for the backbone polymer glass transition supports the combination of these linear polyester molecules, resulting in the loss of small MW portions of resins acting as placticizer in this high-solids coating system. This leads apparently to an increase in the absolute viscosity value, while the coating's rheology remains unaffected because the linear polymer molecules are still dominating. A relatively quicker stabilizing of viscosity increase exhibited in the pigmented systems is due to the spatial separations made by the large volume of pigment particles dispersions, which would have considerably slowed down any reaction at room temperature.

Still another possibility lies in the acid catalyzed self-condensation reactions of melamine crosslinker, as reported by some researchers[27] and our previous studies in the polyester model ISPC.[10] Again it is not likely that this reaction will develop to any significant extent where microgels of melamine cluster are formed, as such formation would have affected the coating's rheology. On the other hand, such reactions lead to the consumption of amino functional groups of the crosslinker, resulting possibly in a cured film with lowered crosslinking density. This is not found in our thermal analysis for the cured ISPC films using the coating formula after eight weeks of storage. Conclusively, the ISPC formula shows an initial increase in absolute viscosity at room temperature, owing most probably to the acid catalyzed polymer chain extension of polyester molecules in the formula. This is a classic problem with melamine baking enamels, and usually requires the addition of a volatile base to temporarily neutralize the acid.[24]

CONCLUSION

For the first time, a new technique of in-situ phosphatizing coating has been applied to form a high-solids formula of polyester-melamine baking enamel. Pencil hardness, tape adhesion, and T_g measurements show that the cured paint films of control MCCS and modified ISPC are very similar. Both EIS and standard corrosion tests show advantageous corrosion resistance properties for ISPC. A slower rate of cathodic delamination is indicative of an enhanced paint adhesion for ISPC. It is shown that ISPC can provide appreciably better performance on regular iron phosphated substrates than standard multi-step coating of MCCS, making it a potential candidate for the substitution of environmentally unfriendly chromate (Cr^{6+}) post-treatment. The results also suggest that ISPC is capable of achieving equivalent, if not improved, corrosion protection on bare CRS panels compared to that of the control coating on the iron phosphated substrate. This implies the possibility that, by using this ISPC technique, we may finally eliminate special iron phosphate pre-treatment, saving both energy and chemical resources by discontinuing the phosphating line/bath of the current standard. The high-solids ISPC formula remains perfectly sprayable after 10 weeks of storage at room temperature, although a noticeable viscosity increase from its MCCS base formula is recorded, owing to the coating's polymer chemistry being affected by the ISPRs. The protective performance of ISPC on bare CRS as compared to that of MCCS over zinc phosphated steel is currently under investigation in our laboratory.

ACKNOWLEDGMENT

Financial support from the National Science Foundation, Grant CTS-9312875 and the Illinois Hazardous Waste Research and Information Center, ENR Contract No. RRT19 is acknowledged. The authors would like to express their gratitude to the technical support from Mr. Douglas Scherrer, Mr. James Metro, Mr. Ken Olsen and Mr. Douglas Wolf of The Sherwin-Williams Company, as well as their appreciation for the financial support and sample donation from the company.

References

(1) Perfetti, B.M., "Metal Surface Characteristics Affecting Organic Coatings," *Federation Series on Coatings Technology*, FSCT, Blue Bell, PA, 1994.
(2) Van Waxer, J.R., "Surface Treatment of Metals," in *Phosphorous and Its Compound*, Van Wazer, J.R. (Ed.), Vol. II, Interscience Inc., New York, 1961.
(3) Sankara Narayanan, T.S.N. and Subbaiyan, M., *Metal Finishing*, 91, 89 (1993).
(4) Freeman, B.D., *Phosphating and Metal Pre-treatment: A Guide to Modern Processes and Practice*, Industrial Press, Inc., New York, 1986.
(5) U.S. Patent No. 5,322,870 (June 21, 1994) to Lin, "Additive Package for In-Situ Phosphatizing Paint, Paint and Method."
(6) Lin, C.T., Lin, P., Hsiao, M.W., Meldrum, D.A., and Martin, F.L., "Chemistry of a Single Step Phosphate/Paint System," *Ind. Eng. Chem. Res.*, 31, 424 (1992).
(7) Yu, T., Li, L., and Lin, C.T., "Chemical Affinity of In-Situ Phosphatizing Reagents on Cold-Rolled Steel," *J. Phys. Chem.*, 99, 7613 (1995).
(8) Lin, C.T., Lin, P., and Quitian-Puello, F., "Interfacial Chemistry of a Single-Step Phosphate/Paint System," *Ind. Eng. Chem. Res.*, 32, 818 (1993).
(9) Li, L. and Lin, C.T., "SEM-EDS Investigations of Self-Phosphating Coatings," *Ind. Eng. Chem. Res.*, 33, 3241 (1994).
(10) Yu, T. and Lin, C.T., "The Performance of In-Situ Phosphatizing Reagents in Solvent-Borne Paints," *Ind. Eng. Chem. Res.*, 36, 368 (1997).
(11) Wang, C., Chuang, Y.Y., and Lin, C.T., "In-Situ Phosphatizing Coatings I: An Air-Dried Lacquer System," JOURNAL OF COATINGS TECHNOLOGY, *71*, No. 892, 61 (1999).
(12) Funke, W., "Mechanisms of Protecting Metals by Organic Coatings Against Corrosion," in *Corrosion Protection by Organic Coatings*, Kendig, M.W. and Leidheiser, Jr., H. (Ed.), Electrochemical Proceedings Volume 87-2, The Electrochemical Society Inc., Pennington, NJ, 1987.
(13) Whitten, M.C. and Lin, C.T., "Polymerization Behavior of Polyester-Melamine Enamels Catalzyed by an In-Situ Phosphatizing Reagent," JOURNAL OF COATINGS TECHNOLOGY, submitted for publication.

(14) McKenna, G.B., "Glass Formation and Glassy Behavior," in *Comprehensive Polymer Science*, Vol. II, Allen G. and Berington, J. (Eds.) Pergamon Press, London, 1989.
(15) Mathot, V.B.F., "Temperature Dependence of Some Thermodynamic Functions for Amorphous and Semicrystalline Polymers," *Polymer*, 25, 579 (1984).
(16) Montserrat, S., "Effect of Crosslinking Density on $\Delta C_{p(Tg)}$ in an Epoxy Network," *Polymer*, 36, 435 (1995).
(17) Bershtein, V.A. and Egorov, V.M., *Differential Scanning Calorimetry of Polymers: Physics, Chemistry, Analysis and Technology*, Kemp, T.J. (Translation Editor), Ellis Horwood, Inc., New York, 1994.
(18) Hepburn, B.J., Gowers, K.R. and Scantlebury, J.D., "Interpretation of Low Frequency AC Impedance Data for Organic Coatings on Mild Steel," *Br. Corros. J.*, 21, 105 (1986).
(19) Bretherton, N., Thompson, G.E., and Turgoose, S., "An Electrochemical Investigation of the Development of Phosphate Conversion Coatings," *Corrosion Sci.*, 35, 1297 (1993).
(20) Kendig, M. and Scully, J., "Basic Aspects of Electrochemical Impedance Application for the Life Predication of Organic Coatings on Metals," *Corros.*, 46, 22 (1990).
(21) Meldrum, D.A. and Lin, C.T., "AC Impedance Analysis and Factorial Designs of an In-Situ Phosphatizing Coating," JOURNAL OF COATINGS TECHNOLOGY, *65*, No. 818, 47 (1993).
(22) Walter, G.W., "A Review of Impedance Plot Methods Used for Corrosion Performance Analysis of Painted Metals," *Corrosion Sci.*, 26, 681 (1986).
(23) Horner, M.R. and Boerio, F.J., "Cathodic Delamination of an Epoxy/Polyamide Coating from Steel," *J. Adhesion*, 32, 141 (1990).
(24) Wicks, Z.R. Jr., Jones, F.N., and Pappas, P.S., *Organic Coatings: Science and Technology, Vol. 1, Film Formation, Components, and Appearance*, Wiley-Interscience, Inc., New York, 1992.
(25) Patton, T.C., *Paint Flow and Pigment Dispersion: A Rheological Approach to Coating and Ink Technology*, 2nd Edition, Wiley-Interscience, New York, 1979.
(26) Wolfe, M.S. and Scopazzi, C., "Rheology of Swellable Microgel Dispersions: Influence of Crosslink Density," *J. Colloid & Interface Sci.*, 33, 265 (1989).
(27) Gan, S., Solimeno, R.D., Jones, F.N., and Hill, L.W., "Recent Studies of the Curing of Polyester-Melamine Enamels: Possible Causes of Overbake Softening," *Proc. 16th Waterborne and High-Solids Coatings Symposium*, New Orelans, LA (1989).