Polyester Resin Synthesis Techniques For Achieving Lower VOC And Improved Coating Performance

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For the past several years, the coatings industry has faced the challenge of increased regulation of solvent emissions. Lowering the molecular weight of the polyester resin appears to be a feasible approach to higher-solids coatings. However, studies have shown there is an optimum point in lowering the molecular weight below which the VOC of the enamel actually increases. Typically, one-stage resin cooks are employed, leading to high levels of unreacted monomers and oligomers which are volatilized during VOC determinations.[1] Selectively staging the addition of the polyol to minimize the formation of unwanted products is an important key to quality systems for higher-solids enamels with good physical properties.

INTRODUCTION

The coatings industry is striving to comply with federal, state, and local regulations to minimize air pollution. These regulatory pressures have challenged the coatings chemist to make rapid technology changes characterized by higher solids and lower volatile organic content (VOC) coatings.

The high molecular weight resins that gave such good performance in yesterday's conventional polyester systems require too much solvent for today's low VOC standards, and the systems we call high solids today will not meet tomorrow's demanding VOC requirements.

High-solids coatings are generally defined as having nonvolatiles of approximately 80 wt % or a VOC of 2.8 lbs/gal or less. The high molecular weight polyester resins used in conventional low-solids systems generally cannot be used in high-solids enamels. Using less solvent to increase solids and lower the VOC results in extremely high viscosity solutions with these conventional resin systems. A low viscosity enamel solution is essential for good atomization, leveling, and flowout of the coating.

The use of hot spray techniques, reactive diluents, and solvent optimization, plus the development of high-speed bells and discs have helped to lower VOC, but still leave something to be desired.

At the 1981 Water-Borne and Higher-Solids Coatings Symposium,[2] Stephen Belote discussed the reduction in the molecular weight of polyester resins as a means of achieving higher solids. He noted, however, that a point of diminishing return exists beyond which further reduction in the molecular weight actually causes a decrease in solids. Studies have shown that the levels of unreacted monomers and oligomers increase as the polyester molecular weight decreases using conventional synthesis techniques. These monomers and oligomers are volatilized during baking of the enamel, thus adversely affecting both determined solids and VOC. This earlier work showed that an optimum molecular weight exists for a polyester to give the lowest VOC for the coating.

The work presented here describes a synthesis technique that produces polyester resins with a more optimum molecular weight distribution for high solids/low VOC coatings.

Laboratory work has demonstrated that staging the addition of the polyol during resin synthesis can minimize the presence of unwanted products—both high- and low-molecular-weight fractions—present in the finished resin.

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Table 1—TMPD Glycol-Based Resins

	Equivalents		
	Resin 1 (Control)	Resin 2 (2-Stage TMP)	Resin 3 (Lower MW 2-Stage TMP)
1st Stage			
TMPD glycol	11.96	11.96	12.24
Trimethylolpropane	1.72	0.86	0.88
Isophthalic acid	4.56	4.56	4.38
Adipic acid	4.56	4.56	4.38
2nd Stage			
Trimethylolpropane	—	0.86	0.88

Resins were cooked to an acid number of 10 ± 1.

THEORY

The typical synthesis of polyester coatings resins is a one-stage process where all of the reactants are added during the initial reactor charge. This conventional technique results in a broad molecular-weight distribution which includes both high- and low-molecular-weight fractions. The high-molecular-weight resin fractions raise the viscosity, thereby limiting enamel solids. The low-molecular-weight fractions are detrimental to both coating performance and enamel solids or VOC due to volatilization during cure.[3] The resin fraction that is volatilized is not as effective as solvents at reducing viscosity, yet has to be considered volatile under EPA guidelines.

To maximize solids and performance, it is desirable to eliminate both the high and low fractions from the molecular weight distribution of the resin. No doubt, resin chemists could offer many theories as to the preferential reactions that might occur which are influenced by the polymer stoichiometry. It is apparent that multiple staging the addition of some of the reactants will alter the stoichiometry at different points during synthesis as compared to the standard one-stage technique.

When a triol branching monomer, such as trimethylolpropane (TMP), is used in a resin, the probability is high that a significant level of "tetrol" will be formed if it is all added in the initial charge. A tetrol is two moles of TMP with one mole of diacid. This formation of tetrol has a significant effect on the stoichiometric balance of reactants.

Using the tetrol as a reactant in resin calculations, the weight average values, according to the W.H. Stockmayer equations,[4] are greatly increased and show premature gelation. It was theorized from a statistical approach that addition staging of the TMP branching monomer would minimize the tetrol formation and possibly other high- and low-molecular-weight fractions.

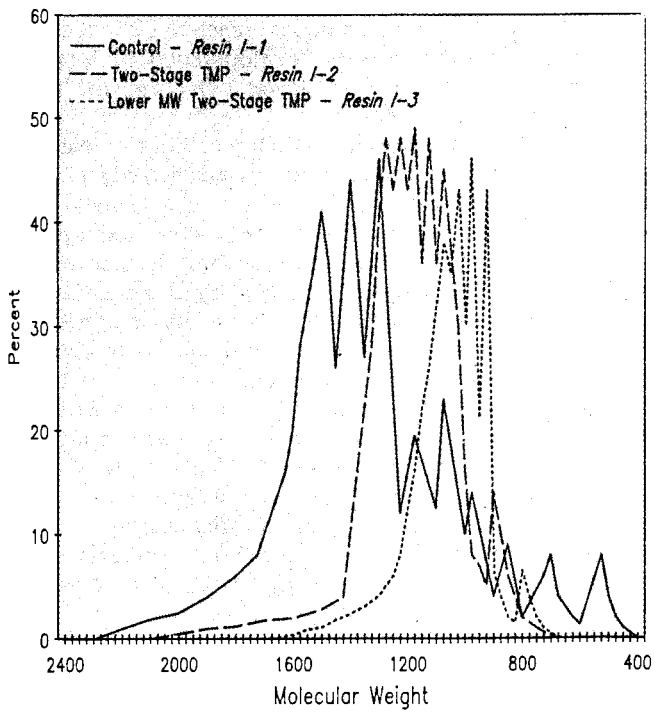

Figure 1—Molecular weight distribution of TMPD glycol-based resins

EXPERIMENTAL

Several types of polyester resins were studied during this detailed laboratory evaluation. Two were selected for the purpose of this report, one based on 2,2,4-trimethyl-1,3-pentanediol (TMPD® glycol) and one on 2,2-dimethyl-1,3-propanediol (NPG® glycol). Both resins utilized trimethylolpropane (TMP) as the branching monomer.

A TMPD glycol-based resin is normally a one-stage cook. All reactants are added initially, followed by nitrogen purge and up-heat to a maximum temperature of 210°C at the end of the synthesis reaction. This is the control resin, Resin 1, in *Table* 1. Resin 2 in *Table* 1 shows the TMP added in two stages (one-half in the first stage and one-half in the second stage), while Resin 3 is a lower-calculated molecular weight resin also two-staging the TMP. In both Resin 2 and Resin 3, the second stage of TMP was added after approximately 50% of the theoretical condensate was collected.

The second resin used in this study is based on NPG glycol. This resin is a two-stage cook because of the dimethyl 1,4-cyclohexane-dicarboxylate (DMCD) and isophthalic acid combination used. To insure a high de-

TMPD and NPG are registered tradenames of Eastman Kodak Co.

Table 2—NPG Glycol-Based Resins

	Equivalents		
	Resin 1 (Control)	Resin 2 (2-Stage TMP)	Resin 3 (Lower MW 2-Stage TMP)
1st Stage			
NPG glycol	25.13	25.13	29.35
Trimethylolpropane	6.65	3.325	1.2
DMCD[a]	10.46	10.46	10.25
2nd Stage			
Isophthalic acid	10.46	10.46	10.25
Trimethylolpropane	—	3.325	1.2

Resins were cooked to an acid number of 10 ± 1.

(a) Dimethyl 1,4-cyclohexanedicarboxylate is a product of Eastman Chemical Products, Inc.

Table 3—Enamels from TMPD Glycol-Based Resins (Calculated Values)

Ingredients	Parts by Weight		
Resin I-1 (85%) in xylene	436.3	—	—
Resin I-2 (85%) in xylene	—	447.1	—
Resin I-3 (85%) in xylene	—	—	454.7
"Cymel" 303 Resin[a]	159.4	163.4	166.2
TiO_2	353.2	362.0	368.1
PTSA catalyst	4.4	4.5	4.6
FC-430 additive[b]	5.5	5.7	5.8
Methyl amyl ketone	110.7	96.5	86.5
Ektapro™ EEP solvent[c]	22.1	22.7	23.1
n-Butanol	22.1	22.7	23.1
	1113.7	1124.5	1132.0
Weight % solids	76.0	77.1	77.9
Volume % solids	61.6	63.2	64.2
Enamel density, lb/gal	11.14	11.25	11.32
VOC, lb volatile/gal paint minus H_2O	2.67	2.57	2.50
VOC, lb volatile/gal solids	4.34	4.07	3.89
Pigment/binder	40/60	40/60	40/60
Polyester/crosslinker	70/30	70/30	70/30
% PTSA catalyst × binder	0.33	0.33	0.33
% FC-430 additive × binder	0.21	0.21	0.21

(a) Product of American Cyanamid Co.
(b) Product of 3M Company.
(c) Product of Eastman Chemical Products, Inc.

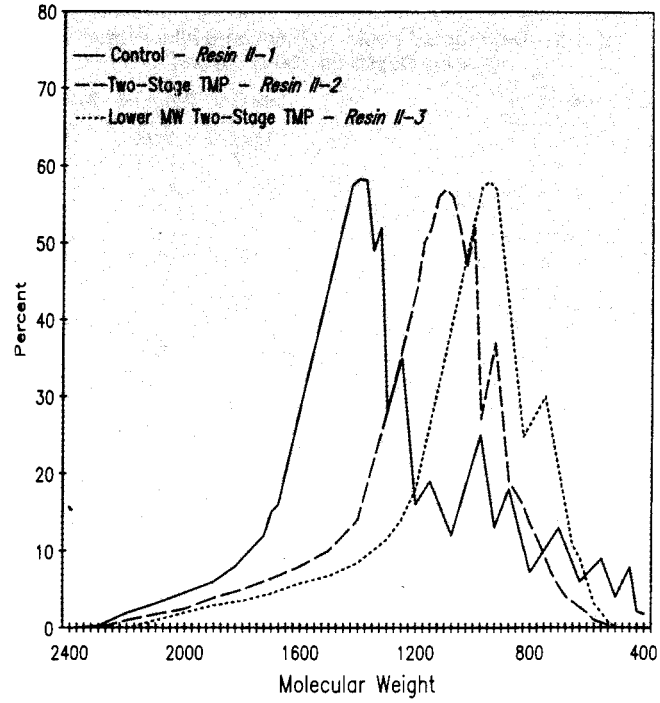

Figure 2—Molecular weight distribution of NPG glycol-based resins

gree of transesterification of the DMCD methyl esters, this intermediate is processed in a first stage reaction with the glycol. In *Table* 2, Resin 1 represents a control product with all of the TMP in the first stage; Resin 2 at the same calculated molecular weight shows one-half of the TMP in the first stage and the other half in the second stage; Resin 3 was calculated to give a lower molecular weight resin which also employs the two-staging technique of TMP addition.

Molecular weight distribution determinations were made by gel permeation chromatography on each synthesized resin. These computer plotted curves are shown in *Figure* 1 for the resins based on TMPD glycol and *Figure* 2 for those based on NPG glycol. Two-staging the TMP in both the TMPD and NPG-based resin systems versus the single-stage controls showed some reduction in average molecular weight, greatly reduced the number and total amount of low-molecular-weight products in the resin, and resulted in a reduced polydispersity (m_w/m_n) in the final resin. These data are shown in *Tables* 5 and 6.

It is known from earlier laboratory evaluations[2] that low-molecular-weight fractions in a coatings polymer adversely affect both enamel solids and physical properties. The elimination of these fractions permits the coatings chemist to improve the enamel physical properties at a higher determined solids. Resin 3 in both *Table* 1 and *Table* 2 shows this optimized resin of reduced molecular weight and two-staging the TMP monomer.

ENAMELS

Enamels were prepared from each resin shown in *Tables* 1 and 2, adjusted to similar viscosities, and evaluated. Enamel formulations, calculated solids, and VOC values are shown in *Table* 3 for TMPD glycol-based resins and *Table* 4 for NPG glycol-based resins.

Staging the TMP monomer gave significant reduction in determined resin viscosity (Resin 2 vs Resin 1) in both TMPD- and NPG-based systems. The lower calculated molecular weight version, which also two-staged the TMP (Resin 3), resulted in the lowest resin viscosity, the narrowest molecular weight distribution range, and a reduced amount of low-molecular-weight fractions. Determined values on the resins, enamels, and cured films are

Table 4—Enamels from NPG Glycol-Based Resins (Calculated Values)

Ingredients	Parts by Weight		
Resin II-1 (80%) in xylene	496.5	—	—
Resin II-2 (80%) in xylene	—	507.3	—
Resin II-3 (80%) in xylene	—	—	525.4
"Cymel" 303 resin	132.2	135.0	139.9
TiO_2	352.8	360.5	373.4
PTSA catalyst (40%)	2.7	2.7	2.8
FC-430 additive (10%)	5.8	5.9	6.1
Methyl amyl ketone	94.9	82.2	60.8
Ektapro EEP solvent	23.0	23.5	24.3
n-Butanol	23.0	23.5	24.3
	1130.9	1140.5	1157.1
Weight % solids	75.3	76.3	77.9
Volume % solids	60.2	61.5	63.7
Enamel density, lb/gal	11.31	11.41	11.57
VOC, lb volatile/gal paint minus H_2O	2.79	2.71	2.56
Pigment/binder	40/60	40/60	40/60
Polyester/crosslinker	75/25	75/25	75/25
% PTSA catalyst × binder	0.20	0.20	0.20
% FC-430 additive × binder	0.22	0.22	0.22

Table 5—Determined Resin, Enamel, and Film Properties (Resins Based on TMPD Glycol)

Resin Properties	Resin I-1	Resin I-2	Resin I-3
M_w (determined)	3886	2374	1555
M_n (determined)	1508	1074	999
Polydispersity M_w/M_n	2.57	2.21	1.56
Gardner viscosity (85%) in xylene	Z_2	Z	X-Y
ICI viscosity (125°C)	1.8	1.6	0.9
OH value (cal)	170	170	185
Enamel Properties			
NV, % by wt (determined)	75.6	76.5	77.6
Viscosity (no. 4 Ford cup), sec	37	34	36
VOC, lbs/gal (determined)	2.72	2.64	2.53
Resin/crosslinker	70/30	70/30	70/30
Film Properties[a]			
Thickness, mils	1.3	1.35	1.5
Impact res. front/reverse, in./lbs	100/20	140/80	140/80
Hardness, pencil	2H	2H	2H
MEK resistance (double rubs)	>200	>200	>200
Cleveland humidity, 48 hrs at 140°F			
Blisters	None	None	None
Gloss, 60°/20°	92/84	90/82	91/82

(a) Coatings were applied to zinc phosphate pretreated CR steel panels.

Table 6—Determined Resin, Enamel, and Film Properties (Resins Based on NPG Glycol)

Resin Properties	Resin II-1	Resin II-2	Resin II-3
M_w (determined)	2886	2007	1555
M_n (determined)	1424	1134	968
Polydispersity M_w/M_n	1.84	1.77	1.64
Gardner viscosity (85%) in xylene	Z_4	Z_3	Z_1
ICI viscosity (125°C)	6.8	5.4	3.2
OH value (cal)	175	175	180
Enamel Properties			
NV, % by wt (determined)	73.1	74.2	77.5
Viscosity (no. 4 Ford cup), sec	37	35	34
VOC, lbs/gal (determined)	2.94	2.82	2.54
Resin/crosslinker	75/25	75/25	75/25
Film Properties[a]			
Thickness, mils	1.2	1.3	1.4
Impact res. front/reverse, in./lbs	100/32	160/140	160/130
Hardness, pencil	4H	4H	4H
MEK resistance (double rubs)	>200	>200	>200
Cleveland humidity, 48 hrs at 120°F			
Blisters	None	None	None
Gloss, 60°/20°	90/81	91/81	91/80

(a) Coatings were applied to zinc phosphate pretreated CR steel panels.

tabulated in *Table* 5 for TMPD glycol resins and *Table* 6 for NPG glycol resins.

In comparing the enamel solution properties after viscosity adjustment, it was quite apparent that staging the TMP in resin synthesis caused significant improvements in enamel solids and VOC.[3] VOC determinations were made using curing time and temperature for the enamels. For the TMPD resin-based enamels, 325°F/20 min was used, while 250°F/20 min was used for NPG glycol resin-based enamels.

In the cured films, the impact resistance was also noticeably improved without sacrificing hardness. This is due to the reduction in low-molecular-weight fractions which are known to adversely affect physical properties as well as the VOC of a coating.[2]

RESULTS

During this evaluation, molecular weight distribution determinations showed conclusively that low-molecular-weight fractions were greatly reduced with multiple additions of TMP branching monomer over a single stage addition. It was also noted in related but unreported work that adding the branching monomer (TMP) in two stages was almost as effective as three or more additions of this material.

The two-stage technique for the addition of the branching monomer allowed for the formulation of lower molecular weight resins which produced higher solids enamels with improved physical properties.

SUMMARY

This work was designed to determine the effect of staging the branching monomer, such as trimethylolpropane (TMP), on resin viscosity, molecular weight distribution, and enamel properties. Two resin types, both using TMP monomer, were reported in this paper from several resins evaluated.

In all cases, two-staging the TMP monomer resulted in a narrower molecular weight range and minimized the amount of low-molecular-weight fractions in the resin. Resin viscosity was greatly reduced, enhancing the VOC properties of the enamels. This staging technique also permitted the formulation of lower molecular weight resins with improved physical properties over systems employing single stage TMP monomer additions.

References

(1) American Cyanamid Publication CRT 178, "Cyanamid Cross-Linking Agents for High Solids Coatings."
(2) Belote, S.N. and Blount, W.W., "Optimizing Resins for Low VOC," JOURNAL OF COATINGS TECHNOLOGY, *53*, No. 681, 33-37 (1981).
(3) EPA Publication EPA-450/2-77-008 (OAQPS No. 1.2-073), May 1977, "Guideline Series—Control of Volatile Organic Emissions from Existing Stationary Surfaces."
(4) Stockmayer, W.H., *J. Chem. Phys.*, *11*, 45 (1943); *12*, 125 (1944).

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