Optimizing Resins for Low VOC

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Volatilization of low molecular weight resins designed for high-solids coatings can cause a significant differential between calculated solids and determined solids of coatings. The resin that is volatilized is not as effective at reducing coatings viscosity as solvents, yet has to be considered volatile under the new EPA guidelines. It was theorized that an optimum average molecular weight exists for a combination of resin raw materials at which VOC at the same viscosity cannot be reduced by lowering resin molecular weight.

Six polyester resins of the same composition but with varying molecular weights were evaluated for VOC at the same viscosity with various catalyst levels and cure temperatures. An optimum molecular weight was determined. It was further determined that the effects of catalyst level and cure temperature on VOC were significant.

INTRODUCTION

The coatings industry has and is continuing to develop high-solids coatings to comply with evolving federal, state, and local air pollution control regulations. For purposes of this work, high-solids coatings are defined as having a nonvolatiles level approaching 75–80 wt% solids or volatile organic compounds (VOC) approaching 2.8 lb/gal of coating. The high-molecular-weight resins used in the binders of conventional low-solids (20–50 wt% solids), solvent-reduced coatings generally cannot be used in the new high-solids coatings. Removing solvent from the conventional coatings formulation achieves high solids or low VOC but results in coatings with extremely high viscosities. For conventional application equipment, a low viscosity is essential for proper application, leveling, and flow of the coatings.

To achieve high-solids coatings at a usable application viscosity, resins had to be developed that do not require as much solvent to reach the desired application viscosity. The obvious method of achieving this goal is to lower the molecular weight or degree of polymerization of the binder resins. A low-molecular-weight resin with lower viscosity should not require as much solvent as a similar high-molecular-weight resin to achieve a sufficiently low viscosity for application of coatings.

Some commercial high-solids resins have been found to partially volatilize during baking at temperatures required for curing amino crosslinking resins.[1] The significant difference in solids is most likely due to the volatilization of the low-molecular-weight fractions of resin or unreacted monomers that have previously been considered as nonvolatile material. This volatilization of fractions reduces the projected higher solids content that was the objective of lowering the resin molecular weight. The EPA Control Technique Guidelines[2] require that the nonvolatiles actually be determined and not simply calculated from the amount of solvent added. Therefore, the resin volatile fractions will be considered the same as organic solvents in the VOC regulations. The organic solvents added to high solids coatings are more effective at reducing solution viscosities than are the volatile resin fractions.

It was theorized that a point of diminishing returns might exist at which lowering the molecular weight of a resin formulation to achieve higher solids does not increase the solids or lower the determined VOC at viscosities required for proper application. Furthermore, the highest possible molecular weight for any given resin is usually optimum for achieving the best overall properties of the cured enamel. The objective of this work was to determine the optimum molecular weight for achieving the lowest VOC independent of coatings

Table 1—Properties of High-Solids Polyester Resins for VOC vs Number Average Molecular Weight

Resin Number	1	2	3	4	5	6
% Excess hydroxyl	15	20	30	52	70	100
Theoretical Mn @ 10 acid number	1255	1005	756	500	401	315
Determined Mn (VPO)[a]	1382	1158	978	728	643	601
Determined Mn (SEC)[b]	1171	949	913	632	585	521
Determined Mw(SEC)	2268	1793	1500	950	800	688
Determined acid number	7	9	7	11	10	4

(a) Vapor Pressure Osmometry.
(b) Size Exclusion Chromatography.
Constants: Composition—NPG® Glycol/Phthalic Anhydride/Adipic Acid Molar Ratio of Phthalic Anhydride/Adipic Acid—3/1
Variables: Excess NPG Glycol Varied to Achieve Range of Molecular Weights

properties of a polyester resin based on NPG® glycol (2,2-dimethyl-1,3-propanediol).

EXPERIMENT

Resin

Six linear polyester resins with the basic composition of NPG glycol, phthalic anhydride, and adipic acid were synthesized in the laboratory, keeping the ratio of phthalic anhydride to adipic acid constant, and varying the excess hydroxyl level to achieve a range of molecular weights (see *Table* 1). The theoretical number average molecular weights (Mn) ranged from 315 to 1255, corre-

sponding to excess hydroxyl levels of 100% to 15%. The Mn values, as determined by the vapor pressure method (VPO), ranged from 600 to about 1400. Mn by size-exclusion chromatography (SEC) ranged from 500 to 1200 and weight-average molecular weight (Mw) from 700 to 2300. All further references to Mn values in this paper are those determined by the VPO method.

A portion of each of the experimental resins was dissolved in xylene to achieve a resin to xylene ratio of 80:20 weight percent. Gardner-Holdt viscosities of the resin solutions were determined. *Figure* 1 shows the effect on viscosity of lowering the Mn of a resin from 1400 to 600 at constant theoretical solids level. As expected, lowering the Mn of the resin resulted in lower viscosities.

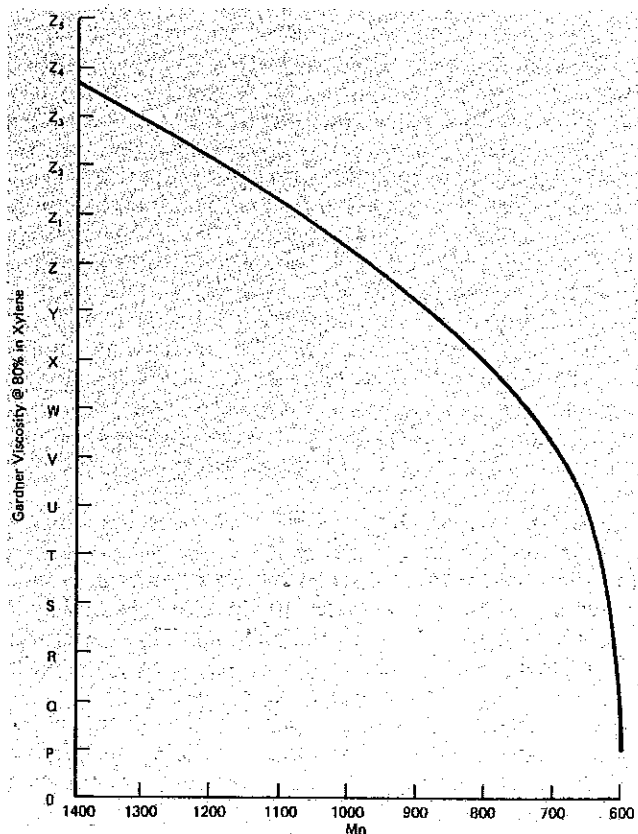The nonvolatiles of the resin/xylene solutions were determined without a crosslinking resin present. The

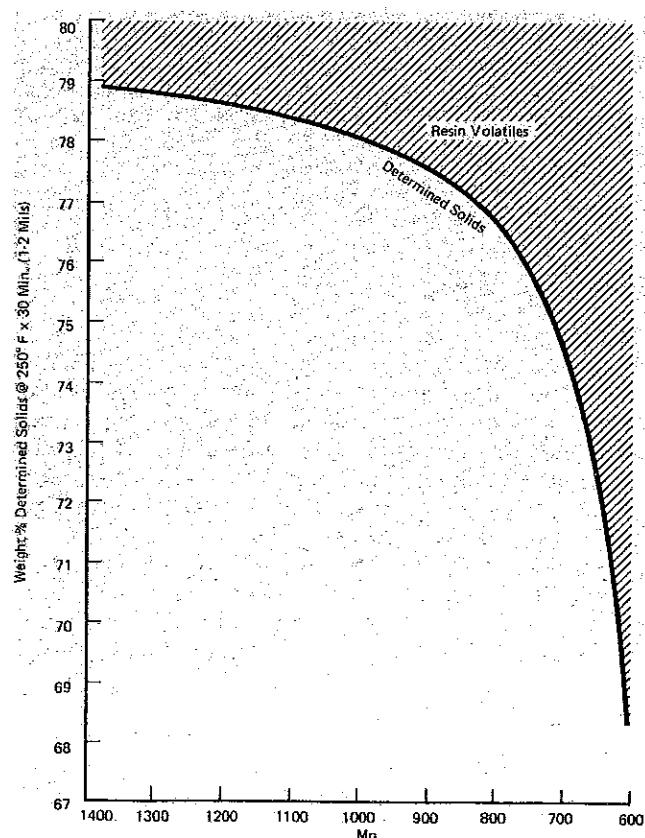Figure 1—Gardner Viscosity vs Mn(VPO). Resin: NPG® Glycol/PA/AD. Theoretically 80.0 wt.% Solids

Figure 2—Determined solids vs Mn(VPO). Resin: NPG® Glycol/PA/AD. Theoretically 80% Solids

method used was a modified version of ASTM D 2369. The nonvolatiles were determined at 121°C (250°F) for 30 minutes with a volume of resin solution sufficient to obtain a dry film thickness of 1–2 mils (25–50 μm). This test is thought to be representative of the actual cure conditions used in a typical amino-resin, crosslinked polyester enamel and representative of the actual VOC emitted from the enamel on a typical surface finishing production line. To achieve a dry 1–2 mil film on the bottom of a 2.75 in. diameter (7 cm) dish, it was calculated that 0.25 cm³ (mL) of solution in the 70% to 80% nonvolatiles range would be required.

Figure 2 shows the effect of lowering the Mn of the resin on the *determined* solids. Reducing the Mn of the resin from 1400 to 600 increased the differential between the determined solids level and the 80% theoretical solids level. The lowest molecular weight resin evaluated (Mn = 600) was determined to be nearly 15% lower in solids than calculated.

The viscosity vs Mn relationship indicated lowest viscosity was achievable with the 600 Mn resin, and the determined solids vs Mn relationship indicated highest solids was achievable with the 1400 Mn resin. To meet new compliance guidelines on nonvolatile content and viscosity requirements for application, both maximum solids and minimum viscosity coatings are desirable. To evaluate the resins while varying only one of these properties, enough xylene solvent was added to each of the original 80/20 resin/solvent solutions so that all were at the same *determined* nonvolatiles; i.e., the same
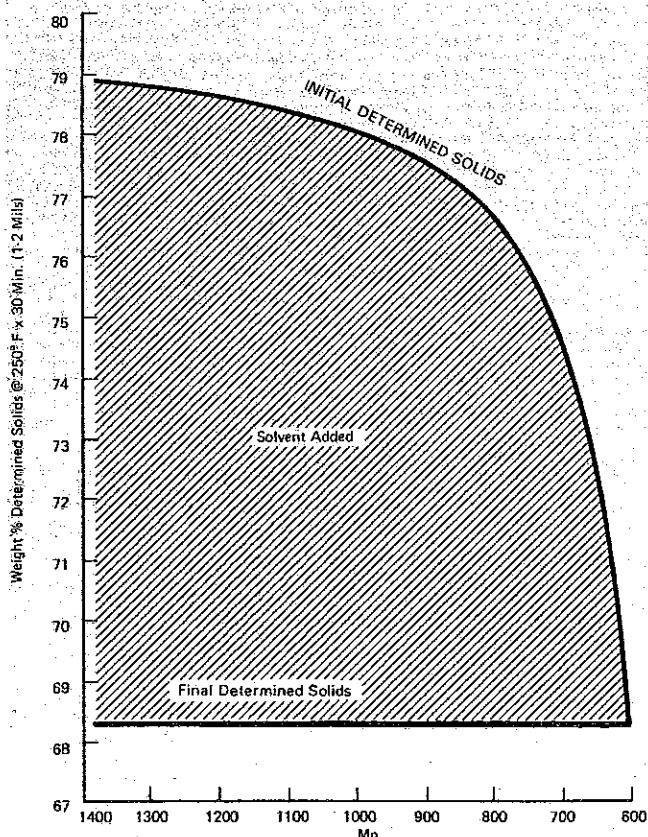
nonvolatile value obtained for the lowest molecular weight resin, or 68.4 wt% (refer to *Figure* 3). With the percent determined nonvolatiles of each resin held constant, the resins could then be evaluated for their effectiveness in high-solids coatings by measuring the viscosity of the resin solutions. Therefore, the resin which gives the lowest viscosity should be the optimum resin for high-solids coatings based on Mn.

Figure 4 shows the viscosity vs the Mn of the resins at the same determined solids. Lowering the Mn from 1400 to 800 significantly lowered the viscosity. Reducing the Mn from 800 to 600 showed an increase in viscosity at the same determined solids.

These responses indicate the validity of the concept of reaching a point of no further reduction in viscosity when lowering the resin Mn at the same determined solids level. A Mn of about 800 appears optimum for a resin based on NPG glycol, phthalic anhydride, and adipic acid for lowest viscosity at the same determined solids level. The 800 Mn resin would be chosen over a lower molecular weight resin because, normally, the higher Mn resins give improved cured enamel performance properties.

Enamel

Fractions of the resins volatilized from the resin solutions described above are probably unreacted glycol or lower-molecular-weight, hydroxyl-containing, polyester oligomers that may be reacted with a melamine crosslinking resin. Thus, some of the volatile resin may

Figure 3—Reduction of resins to same determined solids. Resin: NPG® Glycol/PA/AD. Theoretically 80% Solids
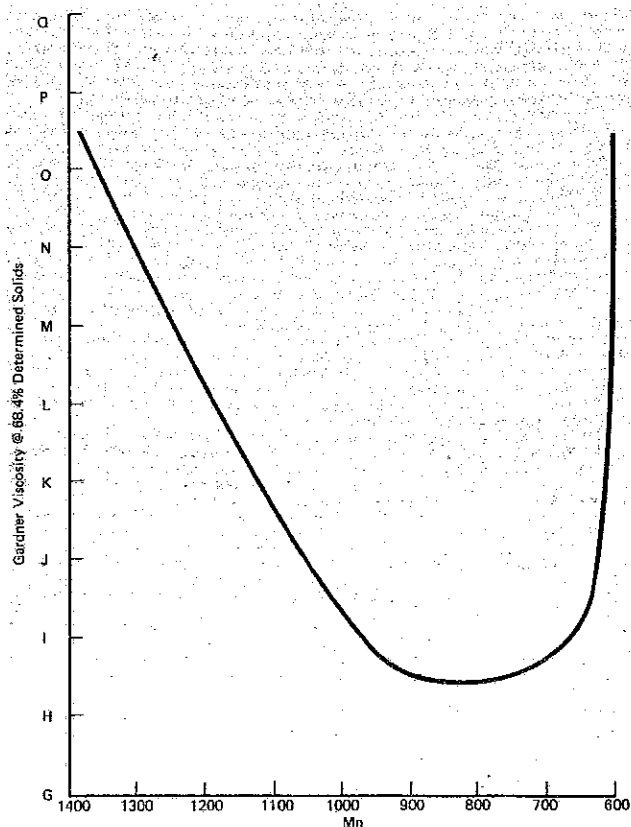
Figure 4—Gardner Viscosity vs Mn (VPO). Resin: NPG® Glycol/PA/AD. Determined 68.4 wt.% Solids

Table 2—Properties of High-Solids Polyester Resins for VOC vs Mn Evaluation

Resin Number	1	2	3	4	5	6
Determined hydroxyl number	72	98	127	151	242	316
Wt % resin solids volatilized	0.99	1.56	2.37	6.94	8.16	14.51
Calculated effective hydroxyl number	62	82	104	82	168	187
% HMMM × binder based on effective hydroxyl number	11	14	17	14	25	27

not be lost when fully formulated enamels are stoved. Therefore, in determining the optimum molecular weight, it is also important to determine the nonvolatiles of the polyester enamels in the presence of the crosslinking resin.

Since cure temperature variations affect the volatility of the low-molecular-weight fractions of resin, both a high-bake (163°C, 325°F) enamel and a low-bake (121°C, 250°F) enamel were investigated. For the high-bake enamels, 0.3% p-toluenesulfonic acid based on binder was adequate to achieve complete cure of these resins with the hexamethoxymethylmelamine (HMMM) crosslinking resin. Cure of the enamels was considered complete when the films resisted softening in contact with acetone. To achieve cure of the low-bake enamels, 1.0% of a pyridine blocked catalyst was necessary to ensure acceptable viscosity stability of the enamels.[3]

Because the ratio of polyester to HMMM is important in evaluating resin volatility, two enamel experiments were done. In the first experiment, an attempt was made to formulate the hydroxyl bearing polyester and HMMM

crosslinker on a stoichiometric basis. This meant a different HMMM level for each resin. In the second enamel experiment designed as a control for the first, a constant polyester/HMMM ratio was used.

In the first enamel experiment, several assumptions were made. Perhaps the most difficult assumption made was the equivalent weight or functionality of the HMMM resin. This subject has been explored by several researchers.[1,4] The functionality of HMMM is not constant. Santer and Anderson reported that the functionality of HMMM which theoretically approaches six, depends on temperature of cure, level, and type of functionality of the vehicle, ratio of vehicle to HMMM, and catalysis.[4] As a practical matter, the functionality is thought to be between three and four for conditions encountered in this experiment. An equivalent weight of 111 was used in calculating stoichiometric vehicle ratios. The second assumption needed for the first enamel experiment was the method for calculating each polyester resin's equivalent weight per *available* reactive hydroxyl group. Since the loss of a portion of the lower molecular
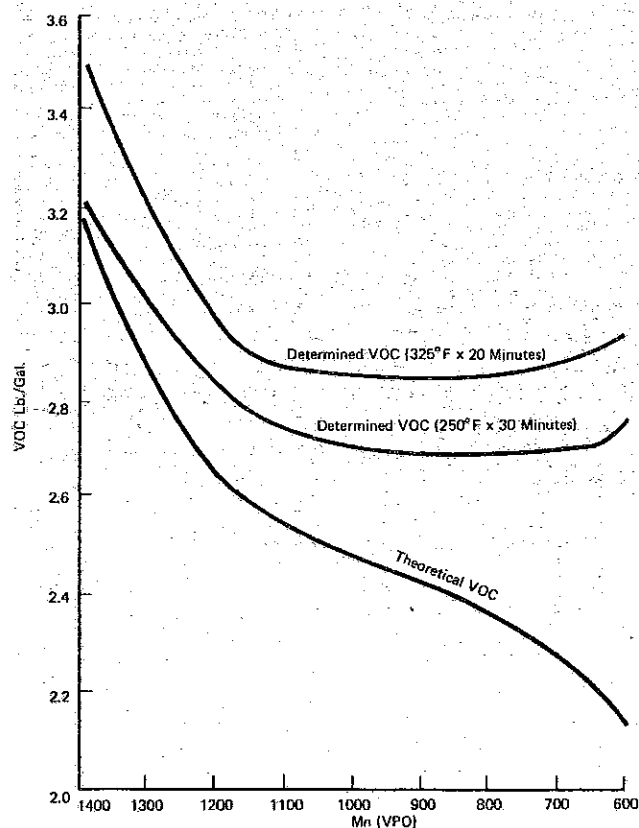

Figure 5—VOC vs Mn (VPO). NPG® Glycol/PA/AD Resin Based Enamels at Eff. Melamine Level. Viscosity—45–49 Sec. No. 3 Zahn
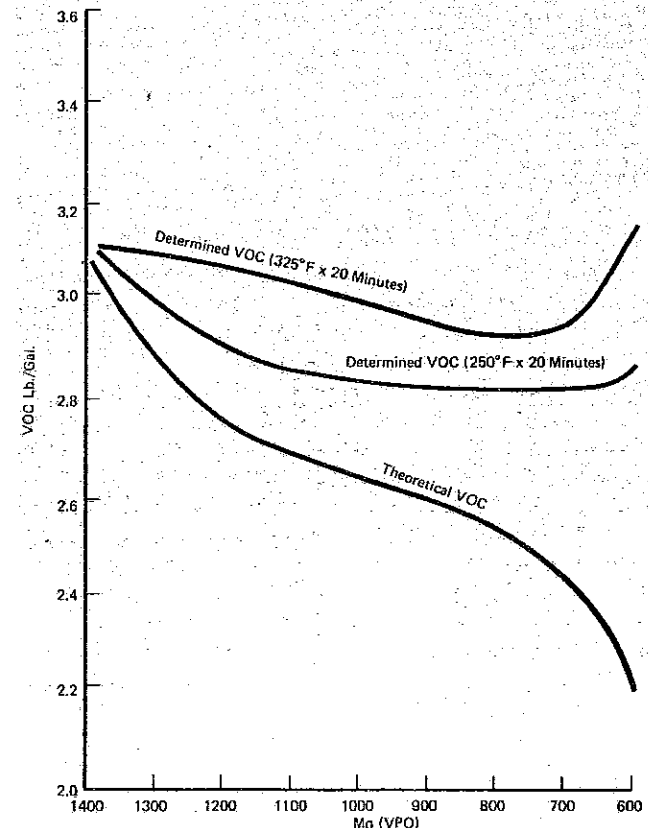

Figure 6—VOC vs Mn (VPO). NPG® Glycol/PA/AD Resin Based Enamels at 20% Melamine Level. Viscosity—34–38 Sec. No. 3 Zahn

weight resins during baking of the enamels changes the effective hydroxyl number of the resin, adjustment of the resin determined hydroxyl number was required.

As discussed previously, this lost material may or may not be volatilized during cure in the presence of a cross-linking resin. Only for purposes of determining each resin's effective equivalent weight, the weight of resin lost in the nonvolatiles determination was assumed to be lost in the enamels and also assumed to be unreacted glycol. With these assumptions and data, the effective hydroxyl number was calculated (see *Table* 2).

Using the calculated effective hydroxyl number for the polyester resin resulted in a polyester/HMMM weight ratio range of 73/27 to 89/11 to be used in the first enamel nonvolatile determination experiment. The second experiment was designed using a constant 80/20 weight ratio of polyester/HMMM to help ensure that any conclusions drawn would be the result of differences in the polyester resins and not differences in melamine crosslinker levels.

The enamels prepared from each resin using the calculated effective HMMM level were formulated to a No. 3 Zahn viscosity of 47 ± 2 seconds (approximately 400 cP). Enamel nonvolatiles or fraction volatiles were determined by the test method discussed earlier. The density of each enamel was determined using ASTM D 1475. The data was used in equation (1) to arrive at the determined VOC of each enamel.

$$\text{VOC (lb/gal)} = \text{enamel density (lb/gal)} \times \text{fraction volatiles of enamel} \quad (1)$$

In addition, the theoretical VOC was calculated from each enamel formulation using the determined density of the enamels and assuming the HMMM resin to be 75% solids. Previous work by the authors has shown that during cure, at least a 25% weight loss results from the liberation of by-products from the crosslinking reaction, predominately methanol.

RESULTS

Variable Polyester/Melamine Ratio

Figure 5 shows the relationship between the *determined* VOC at two cure temperatures and the *theoretical* VOC utilizing the calculated, effective HMMM level. The HMMM level increases as the molecular weight of the resins in the enamels is lowered.

When the molecular weight of the resin is lowered, the *theoretical* VOC is continuously decreased. The *determined* VOC values at both temperatures are reduced as the molecular weight is lowered from 1400 to 1000, then these VOC values do not change significantly from 1000 to 650 before increasing between 650 and 600. As the Mn decreases, apparently enough of the resin is lost in the presence of a crosslinker to show the same general effect that occurred without the crosslinker: i.e., that an optimum molecular weight exists for high-solids coatings. For the NPG glycol/phthalic anhydride/adipic acid resin, this value is approximately 1000.

Also of importance in *Figure* 5 is the significant difference between the VOC determined at 325°F and the VOC determined at 250°F. The VOC value was 0.2 to 0.3 pounds lower per gallon of paint at a bake temperature of 250°F than at 325°F. Higher solids or lower VOC coatings can be more easily achieved if lower temperature cures are possible.

Constant Polyester/HMMM Ratio

The experiment designed with a constant polyester/HMMM ratio of 80/20 for each resin showed that the effect of lowering Mn to achieve lower VOC was essentially the same and that a Mn of 1000 was optimum for obtaining the lowest determined VOC (see *Figure* 6). As the Mn of the resins is lowered from 1400 to 1000, the VOC of the enamels is reduced. Lowering the Mn from 1000 to 650 has essentially no effect on the VOC, and lowering the Mn from 650 to 600 increases the VOC of the enamel.

This work indicates that a linear polyester based on NPG glycol, phthalic anhydride and adipic acid and having a Mn of 800–1000 or an excess hydroxyl level of about 50 to 30% was optimum for achieving the lowest determined VOC.

DISCUSSION OF OTHER VARIABLES

Other variables normally associated in polyester resin design, such as the type and ratio of acids, the choice of glycols, and the incorporation of polyols to induce branching probably could also affect the optimum Mn for the lowest VOC. The evaluation of these variables was beyond the scope of this experiment, but the possible effect of these resin variables should be considered when formulating a polyester coatings resin. This work details a method of determining the optimum molecular weight for a given combination of raw materials to achieve the lowest determined VOC. The method described may be more important to resin formulators than the optimum Mn value obtained.

SUMMARY

This work was designed to determine the optimum molecular weight of a polyester resin based on NPG glycol, phthalic anhydride, and adipic acid for lowest determined VOC. A series of resins with varying molecular weights were evaluated with and without hexamethoxymethyl melamine crosslinker, but the conclusion was essentially the same. A number-average molecular weight of about 800–1000 or excess hydroxyl level of 50–30% was optimum for achieving lowest VOC.

References

(1) American Cyanamid Publication CRT-178, "Cyanamide Cross-Linking Agents for High Solids Coatings."
(2) EPA Publication EPA-450/2-77-008 (OAQPS No. 1.2-073) May 1977, "Guideline Series—Control of Volatile Organic Emissions from Existing Stationary Sources."
(3) White, Marion M., U.S. Patent 3,474,054, Surface Coating Compositions Containing Pyridine Salts of Aromatic Sulfonic Acids (to the Permalac Corporation), October 21, 1969.
(4) Santer, J.O. and Anderson, G.J., JOURNAL OF COATINGS TECHNOLOGY, 52, No. 667, 33 (1980).