POLYESTER OLIGOMERS OF NARROWED MOLECULAR WEIGHT DISTRIBUTION

Roy C. Williams
Richard M. Benton
Robert S. DeRuiter

Reichhold Chemicals
P.O. Box 13582
Research Triangle Park, NC 27709-3582

ABSTRACT

Attempts to reduce the VOCs in thermosetting solvent borne enamels have led to the use of very low molecular weight polyester oligomers. Unfortunately, traditional polyester preparation techniques leave relatively large amounts of unreacted polyols or polyacids that contribute to VOC, and still produce molecular weight fractions larger than desired. This leads to diminishing returns in VOC reductions. A technique is described to narrow this molecular weight distribution and eliminate low molecular weight residual reactants by a series of alternating stepwise reactions using oxirane and anhydride reactants. The oligomers produced are described and characterized, and their performance in high solids baking enamels reviewed. Difficulties in pigmentation stability in regard to acid catalyst adsorption, gloss and film performance are described as well as corrective techniques for use with these oligomers.

Lack of high molecular weight fractions and possible ionic content from catalyst-polymer bonding cause problems in obtaining high resistivity. Synthetic approaches giving higher aliphatic content in the polyesters which counter this and lead to high resistivity paints are described.

BACKGROUND

Polyester oligomers crosslinked with hexamethoxymethyl-melamine(HMMM) type resins have become increasingly popular as a high solids answer to regulatory demands for lowered volatile organic compound (VOC) coatings. They offer economical baking enamels of low VOCs with an excellent combination of hardness, flexibility and resistance properties. The formula below illustrates such a simple white high gloss baking enamel for spray application.

ILLUSTRATION I

White High Gloss Spray Enamel
Polyester A

Lb.	Gal.	Material
430.80	13.06	Rutile Titanium Dioxide
172.32	19.02	90% Isophthalic Polyester A
21.54	3.19	n-Butanol
64.62	8.91	Xylene
6.46	0.89	Viscosity Suspension and Sag Control Additive
695.74	45.07	
Disperse to 7+ N.S.		
278.58	30.75	90% Isophthalic Polyester A
161.55	16.16	Hexamehoxymethyl melamine
4.06	0.51	p-TSA (40% solution)
0.72	0.09	Anti-Crater Additive
53.85	7.43	Xylene
1194.50	100.01	

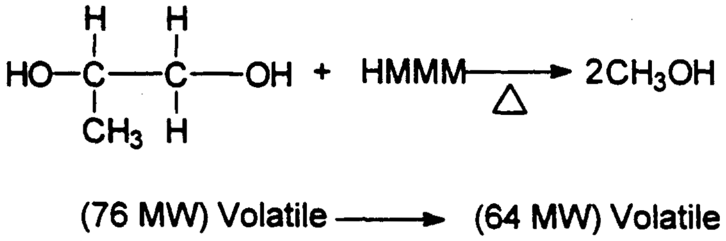
ANALYSIS:

Pigment/Binder Ratio	0.8/1.0
Percent Solids, Weight	81.4
Percent Solids, Volume	69.2
Viscosity at 25°C (approx. Seconds, #4 Ford Cup)	50
Theoretical VOC:	
Pounds/Gallon	1.85
Grams/Liter	222
Determined VOC, via ASTM Method D3960	
Pounds/Gallon	2.57
Grams/Liter	308
Typical Baking Schedule, Min/°F	15-20/300-350

More recently there has been pressure for further VOC reductions; for example, the 2.3 lb/gal or 275 g/l requirements in California. As the above formula illustrates, there is not really a lot (15% by weight) of solvent left which can be removed from these paints. This is especially significant when one considers that a substantial portion of the VOC is alcohols (methanol) evolved from the crosslinking resin, and some low molecular weight esters. This is illustrated by a comparison of the theoretical VOC (solvent evolved) with the determined VOC as measured by ASTM 3960. These crosslinker-derived emissions would represent about 28% of the total from the paint.

To achieve the solvent reduction needed to meet the newer VOC guidelines, one sees one has to remove approximately all of the solvent from the Polyester Oligomer A of the above paint example. This corresponds to approximately an 85% NV white paint as per the above formula. If one further reduces the molecular weight (MW) of the polyester oligomer in an attempt to maintain the same viscosity at the reduced solvent level, the determined NV of the polyester does not rise much above the original 90%. This is due to increased amounts of unreacted and volatile glycols and simple esters. Those function at best as weak solvents. Even anticipating that these would not volatilize from the film because of reaction with the hexamethoxy-methylmelamine (HMMM) resins, they still lead to diminishing returns in terms of emissions. One must consider the reaction of propylene or neopentyl glycol with HMMM and the attendant methanol evolution.

ILLUSTRATION II



$$\mathrm{HO{-}\underset{CH_3}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}OH} + \mathrm{HMMM} \xrightarrow[\Delta]{} 2CH_3OH$$

$$\text{(76 MW) Volatile} \longrightarrow \text{(64 MW) Volatile}$$

Actually, the diminishing VOC returns seen on molecular weight reduction of these oligomers has been long recognized as per the 1981 Journal of Coatings Technology article by Belote and Blount.[1]

As they discussed in their study of a series of neopentyl-adipic-phthalic polyesters of varying molecular weights, little VOC reduction was obtained in going below 1000 MW, as is roughly illustrated below:

TABLE I

Mn	Theoretical VOC	Determined VOC @ 325°F	Determined VOC @ 250°F
1400	3.2	3.5	3.2
1200	2.6	3.0	2.8
1000	2.5	2.9	2.7
800	2.4	2.9	2.7
600	2.2	2.9	2.7

Generally this type of phenomenon is noted with the wide variety of polyester oligomers used in these coatings.

CONSIDERATION OF THE MOLECULAR WEIGHT DISTRIBUTION

Since the molecular weight of these oligomers is low and little is gained by any further molecular weight reduction, one is led to consider viscosity improvements by manipulation of the molecular weight distribution. A technique for doing this is discussed below.

NARROWED MOLECULAR WEIGHT DISTRIBUTION TECHNIQUES

The use of certain polyols such as 2,2,4-trimethyl-1,3-pentanediol, having hydroxyl functionalities of unequal reactivity, can provide self limiting polyester chain growth if carefully balanced with other polyols.

ALTERNATING STEPWISE REACTION APPROACH

A recognized approach to controlling the molecular weight distribution of such polyester oligomers is to prepare them in a stepwise fashion at temperatures below those resulting in transesterification reactions which could broaden the distribution. Ordinarily, one would not do this in polyesterification reactions due to the time involved in the many steps. The low molecular weights desired in the oligomers, however, makes the approach feasible. One would employ a reactant in each step capable of rapidly reacting to completion at lower temperatures. Thus, one would alternate the different reactants in each subsequent step such that the new reactant is only reactive with the resultant functionality derived in the prior step, but not with functionality derived from its own reaction. Thus it theoretically becomes possible to force the reaction of every initial molecule one time. This is done by balancing the number of moles of reactant with the equivalents of reactive functionality on the molecule derived in the prior step and carrying the reaction to completion. The alternation of steps insures that all the molecules are increased in size only by the increment derived from the reactant and thus remain theoretically identical.

Fortunately, two common reaction types offer possibilities for carrying out this approach. These are the half ester reaction of an anhydride with hydroxyl yielding a carboxyl group, and the oxirane reaction with carboxyls liberating a hydroxyl. Both can be carried out at 120°C in one to four hours depending on catalysts chosen.

Since it is desired to build oligomers with functionalities of two or greater, the reaction would be initiated with a multifunctional molecule. The reaction sequence could thus be seen in Illustration III with suitable abbreviations.

ILLUSTRATION III

		M.W.
Initiator	HO-R-OH	76
+2 Anhydrides (Anh)	HOOC - Anh-R-Anh - COOH	372
+2 Oxiranes (Ox)	HO - Ox-Anh-R-Anh-Ox - OH	488
+2 Anhydries	HOOC - Anh-Ox-Anh-R-Anh-Ox-Anh - COOH	784
+2 Oxiranes	HO - Ox-Anh-Ox-Anh-R-Anh Ox-Anh-Ox - OH	900

Since the number of steps is relatively small to build oligomers of the molecular weight desired for these low VOC coatings, and the time of each step relatively short, the economics is not disturbed by lengthy reaction times. The reaction sequence described above would entail about twelve hours, comparable to conventional polyesterification reaction times.

The immediate question is, whether such a scheme can indeed give oligomers free of side reactions and of very narrow molecular weight distribution. To investigate this, we prepared an oligomer from succinic anhydride and cyclohexene oxide (CHOx) using an adipic acid initiator in five steps (Illustration IV). The results are listed in Tables II and III.

ILLUSTRATION IV

Step 1: 2 moles of cyclohexane oxide (CHOx) reacted with 1 mole of adipic acid (AdA), yielding

HO-CHOx-AdA-CHOx-OH (342 MW)

Step 2: 2 moles of succinic anhydride (SU) added yielding

HOOC-SU-CHOx-AdA-CHOx-SU-COOH (542 MW)

Step 3: 2 moles of cyclohexane oxide added, yielding

HO-CHOx-SU-CHOx-AdA-CHOx-SU-CHOx-OH (738 MW)

Step 4: 2 moles of succinic anhydride added, yielding

HOOC-SU-CHOx-SU-CHOx-AdA-CHOx-SU-CHOx-SU-COOH (938 MW)

Step 5 2 moles of cyclohexane oxide, yielding

HO-CHOx-SU-CHOx-SU-CHOx-AdA-CHOx-SU-CHOx-SU-CHO-OH (1134 MW)

TABLE II

GPC Results

Cyclohexane Oxide-Succinic Anhydride Oligomerization (Against Polystyrene Standards)

Step	Theo. Mn	Mn	Mw	Pd
1	342	325	344	1.06
2	542	500	554	1.11
3	738	691	803	1.16
4	938	845	943	1.12
5	1134	1067	1175	1.10
Conventional	1134	1163	2445	2.10

Indeed, the results indicate very narrow molecular weight distributions are possible.

TABLE III

90% Oligomer in Ethoxyethyl Propionate

	Oxirane Anhydride	Random Polyesterification
Step 1 (342 MW)	26 Stokes	---
Step 3 (738 MW)	649 Stokes	---
Step 5 (1134 MW)	7300 Stokes	---
80% Solution	49 Stokes	>150 Stokes

USE OF THE TECHNIQUE

Fortunately, there are a good number of economical oxiranes and anhydrides which can be used to custom design a wide variety of oligomers of different molecular weights and compositions. Oligomer compositions can be prepared while varying the potential film hardness from aromatic content, potential flexibility from aliphatic content, reactivity from end group functionality (hydroxyl-carboxyl), etc. While higher molecular weight materials can be prepared, those most suitable for coatings VOC reduction generally consist of three to five steps.

When different anhydrides or oxiranes are used in preparing oligomers, they can be used in separated steps to keep molecular uniformity. Thus, different reactants can be kept at the same position on the oligomer chains, and in the same molar ratio in each chain. For convenience, they may also be mixed in the same step, which can yield several similar species differing in composition but relatively close in molecular weight and average viscosity. For example, one might use an equimolar mixture of phthalic and succinic anhydrides in the second step of a three step procedure.

PROPYLENE PHTHALATE ADIPATE OLIGOMERS

The GPC data below represents an economical propylene phthalate adipate oligomer synthesized by a similar route. It is an oligomer with a molar ratio of 4 polyols to 3 poly acids.

A polyester oligomer of essentially the same molar composition was prepared in a simple, one-step polyesterification process by replacing the propylene oxide with propylene glycol. Water was removed via a packed-column condenser at 410°F. Viscosity, nonvolatile and GPC comparisons were run on the two oligomers (Table IV).

TABLE IV

	Propylene Oxide 3-Step Oligomer	One-Step Oligomer
Nonvolatile	94%	92%
95% Viscosity in EEP	227	404
GPC Results		
Mn (PS)	863	959
Mw (PS)	1136	1686
Pd (PS)	1.31	1.76

ENAMEL FORMULATION

The reduced molecular weight, narrowed polydispersity, and subsequent reduced viscosity of these resins, allow enamels to be formulated with significantly lower VOC. For example, a simple white high gloss baking enamel with the 90% isophthalic Polyester A yields a determined enamel VOC of 2.6 lbs/gal. In the same formula, two of the reduced polydispersity, propylene adipate phthalate type polyesters, AR2 and AR3, are used. Their respective enamel determined VOCs are 2.4 and 2.1 lbs/gal, at the same viscosity. Table V shows the physical properties of the white enamel films for Polyester A, Polyester AR2 and Polyester AR3.

TABLE V

Comparison of Conventional and Stepwise Polyesters

Enamel Properties	Isophthalic Polyester A	Polyester AR2	Polyester AR3
Viscosity, #4 Ford cup (sec.)	40 - 50	40 - 50	40 - 50
det. VOC, lbs/gal	2.6	2.4	2.1
Film Properties			
(Baked 20 min. @ 350°F)			
Pencil Hardness	4H	4H	3H
Impact (direct/reverse)	60/20	60/20	60/20
60°/20° Gloss	94/80	78/38	70/24
Crosshatch Adhesion, 0 - 5, 5=best	5	5	5
"b" Value Color	-0.2	-0.4	0.0

The properties are quite similar except for the gloss values. The lower values observed for the AR2 and AR3 films forced a closer examination as to how these polyesters respond to common polyester formulating techniques.

It was realized that lowering both the molecular weight and the polydispersity of these resins caused them to behave differently, compared to the 90% isophthalic Polyester A. Specifically, the resins showed differences in both the grinding and the letdown phases of preparation. Consequently, differences were observed in the appearances of the films that were formed. By measuring film properties, both physically and analytically, much was learned about the nature and extent of the differences that these resins showed in response to simple formulating techniques versus Polyester A. As these phenomena were understood, changes in the formulation were made, and these are reviewed in the following sections.

SPECULAR GLOSS

As indicated in the previous section, it was immediately observed that substituting the lower molecular weight polyesters AR2 and AR3, into the simple gloss white formula, produced films with a lower 60°/20° gloss reading than Polyester A. There are several possible reasons for this. First, overcatalysis - which could cause some areas of the film to cure faster than others ("hot spots"). This, in turn, could cause uneven film formation yielding surface defects. Second - catalyst incompatibility - which could cause pigment flocculation, which reduces gloss.[2] Third, poor pigment dispersion - perhaps the result of poor wetting ability of the resins. Fourth, pigment de-wetting during baking - leading to flocculation during cure.

Experimental testing to the conclusion that the initiator was the main problem. The addition of 0.1% of dimethyl ethanol amine (DMEA) improved the gloss.

Scanning electron micrographs were taken of films both with and without DMEA. The high gloss, DMEA containing film was smooth. The low gloss, non-DMEA containing film appeared rough, with definite signs of Benard cell formation. Both of these observations indicate an unstable pigment dispersion and possible flocculation, which lower gloss.[3]

Hence, this small amount of DMEA yields high gloss films by either blocking the catalyst, and/or stabilizing the pigment dispersion. Yet, even though DMEA addition increases gloss, the flow and leveling of the enamel are not as good as Polyester A. Various slower evaporating solvents were also tested to improve gloss and low, but the same low gloss and marginal flow were observed.

CURE STABILITY

As the molecular weight of the polyester was further lowered, from Polyester AR2 to Polyester AR3, the importance of the pigment dispersion phase became more significant. Evidence for this came from the cure stability data. Immediately after preparation, a film of the Polyester A4 enamel cured to an F pencil hardness when baked 15' at 300°F. However, after 24 hours, the same enamel would only cure to a 3B hardness. As time went on, the enamel cured to lower and lower hardnesses, until only a tacky wet film resulted after baking. This indicated that perhaps the curing catalyst was becoming deactivated. The polyester/TiO_2 dispersion was not sufficiently stable, leading to catalyst adsorption and rendering the enamel incapable of producing a cured, hard film. Such pigment-catalyst interactions have been previously reported.[4]

To remedy this, many pigment dispersants were tested to attempt to eliminate the pigment-catalyst interactions. Of the 30 dispersants tested, only dioctyl sodium sulfosuccinate (DOSS) provided a system with good cure stability, as demonstrated in Table VI.

TABLE VI

Cure Stability on Aging of AR3 White Enamels
Baked 15 min @ 300°F

		Film Hardness		
Catalyst System	Det. VOC (lb/gal)	Initial Bake Out	24-Hour Bake Out	7-Day Bake Out
p-TSA	2.00	<5B	<5B	Tacky Film
p-TSA/DOSS	2.15	H	H	H
p-TSA/DDBSA	2.20	H	H	H

The reason that only DOSS is effective at stabilizing the cure is complex. At first it was felt that it improved and stabilized the pigment dispersion. The DOSS could preferentially wet the pigment surface and remain there to prevent catalyst adsorption in the can. Also, it may remain on the pigment surface to prevent any de-wetting and subsequent catalyst adsorption that may occur during baking. Although this may be partially true, the gloss values remained low, and the flow and leveling properties still gave indications of partial flocculation. The improvement in cure properties was related to the strong acid group contained in the surfactant.

DISPERSION STABILITY

Although DOSS, DNNSA, DDBSA and the amine blocked catalysts impart cure stability to the enamel, they may not aid in pigment dispersion stability. Initially the dispersions show a 7.5 + N.S. Hegman reading and appear glossy, which indicate a good dispersion. However, the cured films have low gloss, marginal flow and leveling, and very noticeable orange peeling. These are all signs of poor dispersion stability. This instability can occur either in the can (room temperature storage), during the shear of spraying, or during the baking process. Yet, it must be remembered that both the higher and lower molecular weight fractions that are characteristic of conventional high solids polyesters have been removed. Evidently the absence of these fractions detracts from the ability of the resin to produce a stable dispersion. Since the commercially available dispersants proved ineffective, it was thought that replacing some of the polyester oligomer with a small percentage of a higher molecular weight, better dispersing resin, would help stabilize the dispersion.

Many types of resins that were known to give excellent dispersions were tested. Two of these, an acrylic (AC1) and a coconut alkyd (AL1) were found to give excellent dispersions. Table VII shows the properties of each of these resins.

TABLE VII

Resin Properties of Coconut Alkyd - AL1 and Acrylic AC1

	AL1	AC1
Resin NV - Percent Solids, Wt.	60	69 - 71
Resin Visc. Stokes	36 - 64	98 - 148
Color	3 max.	5 max.
Specific Gravity 25°C/25°C	---	1.04 - 1.06
Pounds/Gallon, solution	8.7	8.7
Acid Value, on solids	6 - 10	60 - 70
Hydroxyl Value	90 - 110	33
Solvent	xylene	2-butoxy-ethanol
MW	17,391	15,882
MN	2,346	4,815
PD	7.41	3.30

In addition to stable dispersions, these resins also imparted cure stability, excellent flow and leveling, high gloss, minimal orange peel and high depth of image (DOI). Also, scanning electron micrographs (SEM) of films with the coconut alkyd versus ones without it show a smooth film versus a bumpy one. X-ray analysis of these same surfaces show well dispersed titanium in the coconut alkyd containing film, whereas the film without it shows that the bumps contain flocculates of titanium. Tables VIII and IX show the cure stability and gloss improvements over the system without these.

TABLE VIII

Cure Stability of AR3 versus AR3 + AL1, and AR3 + AC1

	15 Min @ 300°F Pencil Hardness			20 Min @ 350°F Pencil Hardness		
Resin	Initial Bakeout	24-Hour Bakeout	4-Weeks Bakeout	Initial Bakeout	24-Hour Bakeout	4-Weeks Bakeout
AR3	5B	<5B	<5B	4H	4H	4H
AR3 + AL1	H	H	H	4H	4H	4H
AR3 + AC1	H	H	H	4H	4H	4H

TABLE IX

Film Properties of AR3 versus AR3 + AL1 and AR3 + AC1

	15 Min @ 300°F				20 Min @ 350°F				
Reason	Pencil Hard.	60/20 Gloss	"b" Value Color	Impact Resist.	Pencil Hard.	60/20 Gloss	"b" Value Color	Impact (D/R)	Det. VOC (lb/gal)
AR3	<5B	---	---	---	4H	82/45	+0.1	80/20	2.1
AR3+AL1	H	95/88	-0.8	120/80	4H	96/89	+1.0	80/20	2.3
AR3+AC1	H	94/85	-0.7	100/60	4H	94/81	-0.4	80/20	2.3

Note that even though these higher molecular resins are used as dispersing aids, the VOC of the enamels is still only 2.3 lb/gal, versus the 2.6 value observed for Polyester A.

The high molecular weight of grinding resins can be directly contrasted to the effect of the high molecular weight fractions of Polyester A (2.6 lb/gal). By examining the molecular weight values for all of these resins, a reason for the above observation becomes apparent.

In Polyester A, the MW and MN are 1584 and 824, respectively. Thirty percent of the chains range between 2649 and 5715 molecular weight (21% on total resin solids), and the white enamel VOC is 2.6 lb/gal. For AR3, MW and MN are reduced to 755 and 567, respectively, with 30% of the chains being 1000-2100 molecular weight, which is less than half the value of the high molecular weight fraction in Polyester A. This difference allows the reduction of the VOC from 2.6 lb/gal to 2.1 lb/gal.

In the coconut alkyd, MW is 17,391 and MN is 2346, with 30% of the alkyd ranging 26,000 to 238,000 molecular weight. When used with AR3, only 5-10% on total resin solids is necessary to give the desired enamel properties. This is much less than the 21% of the higher molecular weight, viscosity contributing material that is present in Polyester A. Hence, although the alkyd improves the enamel properties, it only increases the VOC from 2.1 to 2.3 lb/gal, which is less than the 2.6 lb/gal value for Polyester A. The effect with the acrylic is similar. Its MW is 16,000 and MN is 4815, with 30% of the chains ranging 20,000-71,000 molecular weight.

WEATHERING RESISTANCE

While it has been shown that the enamel physical properties of a conventional high solids polyester (isophthalic Polyester A) are not sacrificed when reducing both the molecular weight and the molecular weight distribution, the weathering properties must also be tested.

It is interesting to compare the QUV performance of the lower molecular weight Polyesters AR2 and AR3 with Polyester A. It is believed that poor pigment dispersion stability is responsible for cure and flow deficiencies in AR3 enamels. However, co-grinding with the alkyd (AL1) or acrylic (AC1) improved the flow and cure stability properties significantly. Based on these results, one might also expect the alkyd and the acrylic to improve AR3 QUV resistance. Yet, Table X shows that this is not the case for the alkyd. Contrarily, the acrylic does give noted improvement. This suggests that there may be a difference between how well these resins protect the pigment surface when exposed to QUV. It has been previously shown that the formation of free radicals from the exposed pigment can be one of the most effective catalysts for resin degradation and poor QUV resistance.[5,6] Coconut alkyds, in general, do not perform as well as acrylics in the QUV. This difference is manifested here when they are co-ground into the AR3 enamels.

TABLE X

QUV Yellowing/Gloss Loss Resistance of Gloss White Enamels
Baked 20 Min @ 350°F

	Initial		112 Hours		240 Hours		544 Hours	
Resin	Gloss 60/20	"b" Value Color	Gloss 60/20	"b" Value Color	Gloss 60/20	"b" Value Color	Gloss 60/20	"b" Value Color
AR1	93/78	+0.9	76/63	+1.5	75/32	+2.1	54/12	+1.2
AR2	92/68	+0.5	81/46	+2.4	20/3	+2.9	4/2	+2.7
AR3+DOSS	94/75	+0.8	73/35	+4.3	26/4	+4.6	13/2	+4.3
AR3+AL1	92/72	+1.8	77/40	+2.1	49/12	+2.7	8/2	+2.9
AR3+5% AC1	95/89	+0.7	88/65	+0.9	59/21	+1.1	31/4	+2.0
AR3+10% AC1	94/84	+0.7	88/64	+1.9	63/20	+0.7	27/3	+2.0

RESISTIVITY

The conductivity of a polymer and its solutions is generally described as being directly related to concentration and to mobility of ions passing through it under a charge potential. To minimize conductivity of a polymer solution and maximize its inverse or resistivity, it is desired to decrease the concentration or solubility of ions in it. Also increasing the intrinsic viscosity and thus resistance to ion transport raises the resistivity. The latter, of course, is the opposite of what is needed lower the VOC in paints. Thus, removing the high molecular weight fractions as is the case with the stepwise polymers removes that which contributes most to chain entanglement and intrinsic viscosity.

Thus as is the case with high solids polymers and their paints in general, it was desired to raise resistivity by use of non-polar solvents such as xylene, and to thus minimize the solubility of ions such as those of the acidic catalysts within the paints. These approaches were insufficient in the case of the stepwise polymers such as AR2 and AR3. Resistivity in paints such as the white gloss enamel were still below 0.1 megaohm. The resistivity was considerably lower than would be expected, and this lead to the suspicion that ionic contribution was being made by catalyst residues still bonded to the polyester and thus soluble and conductive in the organic medium.

It was thus desired to raise the resistivity of the stepwise oligomers by use of polyester components which would raise the aliphatic content and provide branching and molecular structure favorable for resistivity. These would also hopefully provide a less favorable media for the solubility of ionic polymeric species.

With the use of branched components inserted into the stepwise oligomers structure, it was possible to prepare paints of high resistivity. In the gloss white enamel formula of the prior illustrations, VOCs below 2.3 lb/gal at 45 sec. #4 Ford Cup were obtained with the oligomers designated AR90 and AR93. Resistivities are on the order of one to three megohms. The paints showed stable cure rates and the resultant films showed high gloss with an excellent combination of hardness and flexibility as well as resistance to accelerated weathering as per Table XI below:

TABLE XI

Oligomers for High Resistivity

	AR90	AR93
NV	97 (1% solvent)	95 (5%)
Viscosity	450 Stokes	250 Stokes
OHV	145	130
White Gloss Formula		
VOC, lb/gal	2.2	2.3
Mega Ohms	2.1	1.5
Viscosity #4 Ford	45 Sec.	45 Sec.
Films 20 Min @ 350°F		
Pencil Hardness	4H	2H
Impact in/lb	60/10	80/20
Gloss 60°/20°	93/83	93/87
After 400 Hrs QUV	67/27	54/18

CONCLUSIONS

The stepwise molecular weight Polyester AR90 is capable of providing an oligomer which will produce films with the same high quality properties as higher molecular weight, lower solids polyesters, at a much lower determined VOC. These low VOCs cannot be achieved by lowering the molecular weights of conventionally produced polyesters. Variations in the properties can be made by the use of pigment dispersants and co-grinding resins. These studies indicate the need for substituting some of the polymer with a better dispersion resin, to obtain the best pigment dispersion, cure stability, flow and leveling, gloss and DOI. This suggests that when removing the low and high molecular weight fractions that are present in conventional high solids polyesters, the resin becomes less capable of giving a stable pigment dispersion.

The regulations are also reported to be changing downward in VOC allowances and it is not clear where they will stop. Table XII below which shows VOC versus paint reduction viscosity indicates that the narrowed molecular weight distribution polyesters maintain or improve their VOC advantage at the higher viscosities.[7,8] The VOC range of 1.3 to 1.5 lb/gal is therefore possible using application equipment designed to spray these higher viscosities. With crosslinkers which would not have emissions by-products VOCs below 1.0 lb/gal might be possible with such equipment.

TABLE XII

VOC vs. Viscosity of Application

Polyester	Trade Name	VOC 50 sec. #4 Ford	VOC 250 sec. #4 Ford
A	Aroplaz 6768 Aroplaz 6755	2.6 lb/gal 2.8 lb/gal	1.9 lb/gal 2.1 lb/gal
AR2		2.3 lb/gal	1.4 lb/gal
AR90	Aroplaz 6820	2.2 lb/gal	1.3 lb/gal
AR93		2.3 lb/gal	1.4 lb/gal

[1] Belote, S.P., and Blount, W.W., "Optimizaing Resins for Low VOC", Journal of Coatings Technology, 53, (681), 33, 81.

[2] Calbo, L.J., "Catalyst Selection for High Solids Coatings", High Solids Coatings, September, 1982, p. 18

[3] Hansen, C.M., "Organic Solvents in High Solids and Water-Reducible Coatings", Progress in Organic Coatings, 10, 331, 82.

[4] Kaluza, U., "Flocculation of Pigments in Paints - Effects and Causes", Progress in Organic Coatings, 10, 289, 82.

[5] Morrison, W.J., Jr., ‘Adsorption of Acid Catalyst onto TiO_2 Pigments", Polymeric Mateirals Science and Engineering, ACS 55, 239, 86.

[6] Volz, H.G., Gunther, K., Fitzky, H.G., "Surface Reactions on Titanium Dioxide Pigments in Paint Films During Weathering", Progress in Organic Coatings, 2, 223, 73/74.

[7] J.O.A.P.S., 37, 1989, pp. 1753-1776.

[8] L. Matejka et al., J. Polym. Sci. Polym. Chem. Ed., 21, 1983, p. 2873.